PB86-138658

Proceedings: Symposium on Flue Gas Desulfurization (9th) Held at Cincinnati, Ohio, June 1985. Volume 2 Sessions 6 through 10 and Appendix

Research Triangle Inst.
Research Triangle Park, NC

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Dec 85

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-138658

EPA/600/9-85/033b
December 1985

PROCEEDINGS: NINTH SYMPOSIUM ON FLUE GAS DESULFURIZATION CINCINNATI, OHIO, JUNE 1985

Volume 2

Sessions 6 through 10 and Appendix

Compiled by

Franklin A. Ayer and Anna W. Wallace

Research Triangle Institute
P. O. Box 12194
Research Triangle Park, NC 27709

EPA Contract 68-02-3992, Task 1

Project Officers:

Julian W. Jones
U.S. Environmental Protection Agency
Air and Energy Engineering Research Laboratory
Research Triangle Park, NC 27711

Stuart M. Dalton
Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94304

Prepared for:

U.S. Environmental Protection Agency
Office of Research and Development
Washington, DC 20460

Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, CA 94304

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/9-85/033b

2.

3. RECIPIENT'S ACCESSION NO. PB86 138658/AS

4. TITLE AND SUBTITLE Ninth Symposium on Flue Gas Desulfurization, Cincinnati, Ohio, June 1985; Volume 2: Sessions 6 through 10 and Appendix.

5. REPORT DATE December 1985

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S) Franklin A. Ayer and Anna W. Wallace (compilers)

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Research Triangle Institute
P.O. Box 12194
Research Triangle Park, North Carolina 27709

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO. 68-02-3992, Task 1

12. SPONSORING AGENCY NAME AND ADDRESS
EPA, Office of Research and Development
Air and Energy Engineering Research Laboratory
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED Proceedings; 6/85

14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES AEERL project officer is Julian W. Jones, Mail Drop 61, 919/541-2489.

16. ABSTRACT

The two-volume proceedings documents presentations at the EPA/EPRI Ninth Symposium on Flue Gas Desulfurization (FGD) in Cincinnati, OH, June 4-7, 1985. The meeting served as a forum for the exchange of technical and regulatory information and developments regarding systems and processes applicable to utility and industrial boilers. Addresses at the opening session: (1) compared regional declines of forests in Europe with those in North America and the possible role of airborne chemicals in these declines; (2) examined the current legislative/regulatory situation; and (3) gave results of a study of the economics of FGD systems in a variety of SO2 reduction strategies for coal-fired power plants. Subsequent technical sessions dealt with new and existing FGD technologies that enabled utility and industrial users of the technology, consultants, engineering firms, equipment manufacturers, process suppliers, government agencies, academia, and research and development firms to share their experiences.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Precipitation	Pollution Control	13B	04B
Flue Gases	Acidification	Stationary Sources	21B	07C
Desulfurization	Reliability	Acid Precipitation	07A, 07D	14D
Forest Trees	Economics	Dual Alkali Systems	06C, 02F	05C
Calcium Carbonates	Spray Drying		07B	13H
Organic Acids	Waste Disposal			

18. DISTRIBUTION STATEMENT Release to Public

19. SECURITY CLASS *(This Report)* Unclassified

20. SECURITY CLASS *(This page)* Unclassified

21. NO. OF PAGES 609

22. PRICE

EPA Form 2220-1 (9-73)

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

These proceedings are of the Ninth Symposium on Flue Gas Desulfurization, held June 4 to 7, 1985, at the Netherland Plaza Hotel in Cincinnati, Ohio. The symposium was cosponsored by EPA's Air and Energy Engineering Research Laboratory (formerly Industrial Environmental Research Laboratory), located in Research Triangle Park, North Carolina, and by EPRI's Coal Combustion Systems Division, located in Palo Alto, California.

The meeting served as a forum for the exchange of technical and regulatory information and developments regarding systems and processes applicable to utility and industrial boilers. Addresses at the opening session (1) compared regional declines of forests in Europe with those of North America and the possible role of airborne chemicals in these declines, (2) examined the current legislative/regulatory situation, and (3) presented results of a study of the economics of FGD systems in a variety of SO_2 reduction strategies for coal-fired power plants. Subsequent technical sessions dealt with the commercial status of FGD in Europe, Japan, and the U.S., limestone FGD/organic acid enhancement, FGD reliability improvement, chemistry/reagent preparation, materials of construction, retrofitting technologies for acid deposition control (panel discussion), dual alkali FGD, emerging technologies, spray dryer FGD, and FGD by-product disposal/utilization.

These proceedings include all of the technical papers presented at the symposium and most of the other presentations. In addition, 8 unpresented technical papers are included.

TABLE OF CONTENTS

VOLUME 1

Page

Session 1: OPENING SESSION 1
Michael A. Maxwell, Chairman

Comparison of Regional Declines of Forests in Europe and North America: The Possible Role of Airborne Chemicals . . . 2
Ellis B. Cowling

Address on Current Legislative/Regulatory Situation 21
Joseph A. Cannon

The Role of FGD in SO_2 Reduction Strategies for Coal-Fired Power Plants 22
E. S. Rubin*, M. Cushey, R. J. Marnicio, C. N. Bloyd, and J. F. Skea

Session 2: COMMERCIAL STATUS OF FGD. 46
Stuart M. Dalton, Chairman

The Present and Future Status of FGD in the United States 47
Robert W. McIlvaine

Survey Report and Assessment of Utility Flue Gas Desulfurization System Installations in Europe. 63
William Ellison

Recent Developments in SO_2 and NO_x Abatement Technology in Japan. 75
Jumpei Ando

EPA's Stationary Source Control Technology Research Program 101
Carl R. Gerber

Session 3: LIMESTONE FGD/ORGANIC ACID ENHANCEMENT. 105
J. David Mobley, Chairman

Results of Using Organic Acid in San Miguel Electric's Flue Gas Desulfurization System 106
Jack M. Burke*, Robert Cmiel, and J. David Mobley

*Denotes speaker

Page

State-of-the-Art Design Applications on a Closed-Loop FGD System. 121
Dennis Laslo* and Even Bakke

Dibasic Acid Test and Chemical Process Evaluation at Petersburg Unit 3 FGD System. 136
D. Guetig, S. Ou, and C. P. Wedig*

Operating Results of Toyama Kyodo Electric Power's Chiyoda Thoroughbred 121 Flue Gas Desulfurization System. 168
K. Wataya, A. Hori, N. Hashimoto, H. Koshizuka, and D. D. Clasen*

Session 4, Part I: FGD RELIABILITY IMPROVEMENT 194
Dorothy A. Stewart, Chairwoman

The Sulfur Dioxide Removal System Improvement Program at Seven Units of Louisville Gas and Electric Company 195
M. L. McInnis, D. A. Froelich, S. A. Bjorklun*, and G. M. Graves

Improving the Reliability of Indianapolis Power & Light Company's Petersburg 3 Limestone FGD System 202
J. David Colley*, Steve Wolsiffer, Dorothy Stewart, Richard Rhudy, and David Balfour

Results of an FGD Process Troubleshooting Program at Texas Utilities, Martin Lake Steam Electric Station 225
David Colley*, Don Mzyk, Mike Wadlington, and Dorothy Stewart

Availability Analyses for Flue Gas Desulfurization Improvement Decisions 247
Albert R. Cunningham* and Morton J. Smith

Session 4, Part II: CHEMISTRY/REAGENT PREPARATION. 260
Dorothy A. Stewart, Chairwoman

A Study of Sulfur-Nitrogen Compounds in Wet Lime/Limestone FGD Systems. 261
James B. Jarvis*, Peter A. Nassos, and Dorothy A. Stewart

Thiosulfate as an Oxidation Inhibitor in Flue Gas Desulfurization Processes: A Review of R&D Results 280
Gary T. Rochelle*, David R. Owens, John C. S. Chang, and Theodore G. Brna

*Denotes speaker

Page

Lime Slaking Using Stirred Mills 302
N. N. Dharmarajan* and R. D. Forbus

Limestone Selection and Preparation for FGD 320
Dorothy Stewart*, J. David Colley,
O. W. (Buddy) Hargrove, and A. J. Jones

Session 5: MATERIALS OF CONSTRUCTION 338
Charles E. Dene, Chairman

Failure Analysis of FGD System Components 339
Gary D. Jones*, Peter F. Ellis II, Dennis M. Anliker,
and Dorothy A. Stewart

Performance of Duct and Stack Materials in Wet FGD Systems. . . . 362
H. S. Rosenberg*, G. H. Koch, C. W. Kistler, Jr.,
J. A. Beavers, M. L. Meadows, and D. A. Stewart

Leaning Brick Chimney Liners at Coal Fired Power Plants 387
E. R. Dille*, D. L. Krueger, and R. G. Rhudy

The Economics of Clad Metallic Fabrication Versus Solid Alloy Metal Fabrication 399
E. H. Cloth* and R. Kreider

Laboratory Evaluation as a Technique for Predicting the Behavior of Organic Coatings in FGD Systems 410
Malcolm L. White*, Henry Leidheiser, Jr., and G. H. Koch

VOLUME 2

Session 6: PANEL DISCUSSION ON RETROFITTING FGD SYSTEMS. 423
Frank T. Princiotta, Chairman

Session 7: DUAL ALKALI 429
Charles B. Sedman, Chairman

Development and Demonstration of a Limestone Dual Alkali FGD Process at Central Illinois Public Service Company's Newton Power Station. 430
Jerry L. Simpson* and James H. Wilhelm

Current Operating Experience and Operating Costs of Double Alkali FGD at NIPSCO's R. M. Schahfer Generating Station Unit 17 441
R. J. Biolchini*, W. L. Boward, Jr., and
B. S. Camponeschi

*Denotes speaker

Page

Current Progress at the FMC Limestone Double Alkali Demonstration Plant 455
Willard L. Boward, Jr.*, Robert J. Biolchini, and Beth A. Wrobel

Effects of Limestone Type and Grind on Dual Alkali System Performance 472
John C. S. Chang*, Theodore G. Brna, and Norman Kaplan

Session 8: EMERGING TECHNOLOGIES 501
Richard G. Rhudy, Chairman

Pilot Evaluation of Combined Particulate and SO$_2$ Removal Using a Fabric Filter System. 502
Richard G. Hooper*, Verle Bland, Franz G. Pohl, Michael McElroy, and Richard Rhudy

Investigation of Combined Particulate and SO$_2$ Using E-SOX 516
Leslie E. Sparks*, Norman Plaks, Geddes H. Ramsey, and Richard E. Valentine

Mitsui-BF Simultaneous SO$_x$ and NO$_x$ Removal System 531
Yoshiro Ito*, T. Fujimoto, and O. Nagaoka

Operating Experiences and Developments with Ljungstroem Gas-Gas Heaters in West German FGD Plants 544
David E. Clay

SOXAL^{tm} Process 559
K. N. Mani* and F. P. Chlanda

Session 9: SPRAY DRYER FGD 579
Theodore G. Brna, Chairman

Spray Dryer FGD Experience: Joy-Niro Installations 580
J. R. Donnelly*, S. Wilson, L. P. Matis, R. Eriksen, R. D. Emerson, and J. C. Fooks

Problem Solving and Results of Performance Test at United Power Association Stanton Station Dry FGD System. 602
Ghassem B. Manavizadeh*, Stefan Negrea, Gordon Westerlind, and Alan W. Ferguson

High-Sulfur Spray Dryer Evaluations 621
Russell F. Robards*, Robert W. Aldred, Thomas A. Burnett, Lynn R. Humphries, and Michael J. Widico

*Denotes speaker

Page

Recent Results from the EPRI 2-1/2 MW Spray Dryer Pilot Plant 643
Richard G. Rhudy and Gary M. Blythe*

Performance of a Spray Dryer/ESP Flue Gas Cleanup System During Testing at the Pittsburgh Energy Technology Center 670
James T. Yeh, Charles J. Drummond, James I. Joubert, Dennis M. Tulenko*, Robert R. Crynack, and Martin L. Hochhauser

Application of Electrostatic Enhancement of Fabric Filtration to Spray Dryer Byproduct 688
L. S. Hovis*, Bobby E. Daniel, Yang-Jen Chen, and R. P. Donovan

Comparison of Pilot Plant Data with Predictions from the U.S. EPA SPRAYMOD Computer Program. 702
Wayne T. Davis*, Gregory D. Reed, George P. Partridge, and Theodore G. Brna

Session 10: FGD BY-PRODUCT DISPOSAL/UTILIZATION. 715
Julian W. Jones, Chairman

Gypsum By-Product FGD System. 716
W. A. Liegois* and D. A. Wicks

By-Product Gypsum Production at a 2300 MW Power Plant 730
Don Myzk and Jan Zmuda
Paper presented by David Holstein

Evaluation of Engineering Properties and Wet Stacking Disposal of Widows Creek FGD Gypsum-Fly Ash Waste 748
John E. Garlanger*, Sal H. Magliente*, Thomas S. Ingra, and James L. Crowe

Solids Handling and Dewatering Optimization at Colorado Ute's Craig Station 767
O. W. (Buddy) Hargrove*, David R. Owens, Dorothy A. Stewart, and Jim Renner

EPRI Research on Management of Wastes From SO_2 Control Processes 785
Dean M. Golden* and Russell H. Boyd

Thermal Oxidation of Spray Dryer FGD Waste Product. 824
S. Bengtsson*, S. Ahman, T. Lillestolen, and G. Koudijs

*Denotes speaker

Page

UNPRESENTED PAPERS 845

Reliability Problems and Solutions of FGD Systems 846
D. C. Agarwal

Four Corners 4 and 5 Waste Processing System: An Integrated and Unique Retrofit. 866
Alexander P. Simko, Richard R. Lunt, and Charles S. White

Corrosion Resistance Comparison of Duplex Stainless Steel with Type 317LM in Simulated Flue Gas Scrubber Environments. 878
Ronald E. Van Hoose and John B. Guernsey

Corrosion Resistance of a Cr-Ni-Mo-Cu-Fe Alloy in Scrubber Environments and Other Chemicals. 889
Terry A. DeBold, Douglas G. Frick, and Gerald A. Bauer

The Chemistry of Sodium Dry Sorbent Injection 902
A. W. Mueller and A. E. Winston

Techno-Economic Investigation Into the Hybrid Technology of FGD and PCC Applied to Large Boilers of Firing Canadian Coals. 922
R. L. Wang

Size Measurements in Aerosols Produced in Sulphur Dioxide Removal by Electron Beams 933
M. D. Carabine, P. G. Clay, and G. Sisniega

The NOXSO Process Development: An Update 948
J. L. Haslbeck and L. G. Neal

APPENDIX: Attendees. 976

PREFACE

These proceedings for the Ninth Symposium on Flue Gas Desulfurization (FGD) constitute the final report submitted to EPA's Air and Energy Engineering Research Laboratory (AEERL), Research Triangle Park, North Carolina, and to the Coal Combustion Systems Division, EPRI, Palo Alto, California. The symposium was conducted at the Netherland Plaza Hotel, in Cincinnati, Ohio, June 4 to 7, 1985.

Almost 600 representatives of electric utilities, state environmental agencies, equipment and process suppliers, coal and petroleum suppliers, architects, engineers, EPA, and other federal agencies, and research organizations attended the symposium.

The following persons were responsible for organizing this symposium:

- Julian W. Jones, Chemical Engineer, U.S. EPA, Air and Energy Engineering Research Laboratory, Gas Cleaning Division, Emissions Technology Branch, Research Triangle Park, North Carolina, was the EPA chairman.

- Stuart M. Dalton, Manager, Reliability and Nonrecovery Systems, EPRI, Coal Combustion Systems Division, Palo Alto, California, was the EPRI chairman.

- Franklin A. Ayer, Consultant, Research Triangle Institute, Research Triangle Park, North Carolina, was the symposium coordinator and compiler of the proceedings.

Session 1: OPENING SESSION

Michael A. Maxwell, Chairman
U.S. Environmental Protection Agency
Research Triangle Park, NC

COMPARISON OF REGIONAL DECLINES OF FORESTS IN EUROPE AND NORTH AMERICA: THE POSSIBLE ROLE OF AIRBORNE CHEMICALS[1]

by Ellis B. Cowling

Associate Dean for Research
and Director of the Acid Deposition Program
School of Forest Resources
North Carolina State University
Raleigh, North Carolina 27695 USA

ABSTRACT

Human activities of many sorts have been changing the chemical climate of Europe and North America especially since the time of the Industrial Revolution. Regional declines of forests also have been occurring in Europe for the past 200 years and in North America for at least the past century. A total of 18 regional declines of forests have been reported on the two continents. These declines are generally believed to be caused by a specific combination of competitional, physical, biological, and chemical stress factors acting simultaneously or sequentially. Airborne chemicals have been implicated as an important causal factor in only four of these 18 cases. A concensus of informed judgement regarding the possible role of selected airborne chemicals is described. This judgement suggests that ozone and biologically available nitrogen compounds are among the chemical stress factors of greatest probable importance to forests. Other chemical stress factors that may also be involved include toxic gases other than ozone, toxic metals, acids, acidifying substances, and growth-altering organic chemicals. Certain implications of this present consensus are discussed briefly with regard to management of air quality in Europe and North America.

---

[1] Many of the ideas described in this summary paper were developed in discussions and observations together with Drs. Peter Schütt, Arthur Johnson, Robert Bruck, Ann Bartuska, Walter Heck, James Galloway, Gene Likens, James Woodman, George Hepting, William Winner, Carl Olof Tamm, Henning Rodhe, Rudolf Husar, Ronald Bradow, Svante Oden, Jack Durham, Paul Manion, David Huston, William Hafley, Donald Marx, Dale Johnson, Steve Lindberg, Peter Rennie, Folke Anderson, Peter Sommers, Hans Martin, Robert Rosenthal, and William Waters. I am very grateful to all of these persons for their contributions to the consensus of informed judgement and other ideas outlined in this paper. Further suggestions for improvement of this summary will be welcome by any scientist who wishes to help advance our present meager understanding of the current declines of forests in Europe and North America.

During the past three decades, scientists, public officials, and industry leaders in Europe and North America have become more and more aware that human activities of many sorts are changing the chemical climate of large regions on both continents. Prior to 1950, pollution of air and water were well known especially because of effects on public health in large cities such as London and Los Angeles. So-called "welfare effects" on aquatic and terrestrial ecosystems were acknowledged, but they were considered to be local events confined almost entirely to the vicinity of metal smelters and other large industrial-urban complexes. Air pollution was considered a local meteorological threat to public health but was not recognized as a regional climatological threat to the productivity or stability of ecosystems. The ideas of long-distance transport of air pollutants and of constant deposition of airborne nutrients and injurious chemicals into aquatics and terrestrial ecosystems were not generally recognized either in science or in public affairs.

To be sure, Angus Smith (1872) had published his magnum opus "Air and Rain: The Beginnings of a Chemical Climatology" nearly a century before. In addition, Erik Eriksson, Christian Junge, and Eville Gorham had published a long series of papers on the linkages between air chemistry and surface water chemistry on both continents (e.g., Eriksson 1952, 1954, 1959, 1960; Gorham 1955, 1957, 1958, 1961; Gorham and Gordon 1960, Junge and Werby 1958). But the work of all these authors was met by a "thundering silence", as Gorham put it so eloquently, until Svante Odén (1967, 1968) published his now famous accusation of an "insidious chemical warfare" among the nations of Europe. Odén's audacious ideas--about the long distance transport of sulfur, nitrogen, and other pollutant chemicals, and especially his predictions of large scale acidification and other changes in surface waters and soils, as well as increased disease in forests--stimulated a veritable storm of public and scientific debate that continues to this day.

Effects on Water Quality, Fish, and Forests

At first, the most important regional-scale effects of airborne chemicals on ecosystems were thought to be the gradual and episodic acidification of sensitive surface waters with attendant effects on fish populations (Hultberg and Stenson 1970, Odén and Ahl 1970, Jensen and Snekvik 1972, Beamish and Harvey 1972). About this same time, the idea of regional-scale accumulation of ozone and other photochemical oxidants was recognized as a possible threat to agricultural crops (NAS 1977) and to certain species of forest trees such as ponderosa and Jeffrey pines in the San Bernardino Mountains of California (Miller and Millecan 1971) and to eastern white pine in the Ohio and Tennessee Valleys of the eastern United States (Berry and Hepting 1964).

In 1963 George Hepting (1963) published his classic paper on the influence of long-term changes in climate on the productivity, health, and stability of forests. Hepting emphasized that long-term climate changes (especially changes in temperature and rainfall patterns) could cause stress in forest trees and other perennial plants just as weather changes cause stress in annual plants. Hepting discussed air pollution in this paper but his strongest point was that changes in the physical climate could effect the health and productivity of forests.

Then, beginning in the late 1970's foresters in many parts of Germany began to see a series of subtle changes in their forests. At first white fir showed renewed signs of an old problem--periodic decline especially of older trees. Later, Norway spruce began to show similar symptoms. And then, all too quickly, it became apparent that nearly every commercialy important species of forest trees were showing evidence of decline in large parts of West Germany and other areas of central Europe. For the first time it appeared likely that airborne chemicals might be among the causal factors involved in a multiple-species decline of forests. Today, we are coming to realize that changes in the chemical climate may be at least as profound in their effects on forests as Hepting (1963) showed was true of changes in the physical climate two decades before.

Objectives

The purpose of this paper is to present a brief summary of the present state of knowledge about regional declines of forests which have occurred in the forests of Europe and North America and to discuss the evidence that various competitional, physical, biological, and chemical stress factors may play a role in these phenomena. This comparison of forest declines in Europe and North America, like an earlier paper on the Waldsterben problem in Europe (Schutt and Cowling 1985), has been written in the hope that it may help attract to the forest decline problems of these two continents, some of the most able minds in plant pathology, plant physiology, soil science, forest ecology, and atmospheric chemistry.

Declines of Forests in Europe and North America

Regional declines of forests are not new. They have been occurring in individual species of trees for at least 200 years in Europe and at least 100 years in North America. At least five regional declines have occurred in Europe and at least 13 other declines in North America during the 20th century. These declines are listed below in approximate order of decreasing relative importance:

Regional declines in Europe:

-- Waldsterben, a multiple species decline of forests in West and East Germany, Czechoslovakia, Austria, Poland, Switzerland, France, Italy, and Sweden. The visible symptoms of Waldsterben were first reported in the late 1970's but its growth effects apparently started in the early 1950's.

-- Tannensterben (white fir decline) in Germany since the middle 1700's.

-- Kiefersterben (Scots pine decline in East Germany and European Russia during the early 1970's.

-- Oak Decline in Germany and especially in France since the early 1900's.

-- Decline of *Pinus pinaster* on the Atlantic coast of France since the early 1980's.

Regional declines in North America:

-- Beech bark disease in the northeastern USA and southeastern Canada since the early 1940's.

-- Littleleaf disease of shorleaf and loblolly pines in the southeastern USA since the early 1920's.

-- Birch dieback in the northeastern USA and southeastern Canada in the early 1940's through the early 1970's.

-- Pole blight of western white pine in the Rocky Mountains of the western USA since the early 1950's.

-- Oak decline in Pennsylvania, Virginia, Texas, Arkansas, and South Carolina since the mid 1960's.

-- Decline of ponderosa and Jeffrey pines in the San Bernardino Mountains of California since the late 1950's.

-- Regional decline of eastern white pine in the eastern USA and Canada since the early 1960's.

-- Several symptomatically distinct maple declines in the northeastern USA and southeastern Canada since the 1950's.

-- Red spruce and Fraser fir decline at high elevation in the Appalachian Mountains of the eastern USA with visible symptoms since the early 1980's and decreased radial growth since the early 1960's.

-- Decline in growth without other visible symptoms in loblolly, shortleaf, and slash pines in the Piedmont regions of Alabama, Georgia, and South and North Carolina since the mid to late 1970's.

-- Ash dieback in the northestern USA and southeastern Canada since the 1950's.

-- Sweetgum blight in the southeastern USA in the 1950's and 1960's.

-- Decline of growth without other visible symptoms in pitch and shortleaf pines in the Pine Barrens region of New Jersey.

Waldsterben in Europe is by far the most important of all the regional declines of forests observed during the present century. This is true for several reasons--the most importance is that Waldsterben is the first multiple-species decline of forests reported in either Europe or North America. In fact, essentially all native and exotic tree species are affected as well as some shrubs and herbs. Waldsterben is also very important because of: a) the large geographical area affected; b) the very great commerical and aesthetic value of the declinng forests to the people of Europe; c) the remarkable diversity of physical, chemical, climatic, soil, site, and forest management conditions in which damage has been observed; and d) the unique symptoms shown by the trees, several of which have never been seen before.

Symptoms of Decline in the Forests of Europe and North America

Careful study and analysis of symptoms is the first and most important step in the identification of the causal factors involved in any disease of living organisms. Table 1 contains a comparison of the major symptoms observed in the declines of forests in Europe and North America. Some of the most important conclusions that can be drawn from this tabulation include the following ideas.

1) The symptoms of decline in forest are diverse and often specific to a particular species of trees.

2) Although there are some similarities, there are many more differences among the symptoms of decline observed in Europe and those observed in North America. This is not surprising since the tree species that are native to Europe are not the same as those in North America. But Norway spruce, which is widely planted as an ornamental tree in North America, is showing nearly identical symptoms of stress on both continents.

3) One of the most important similarities is the tendency for yellowing of foliage to progress from the lower to the upper parts of the canopy and from the inner to the outer portion of branches, oldest tissues affected first. This symptom has been observed on both continents - mainly at high elevation in Europe and in the San Bernardino and Appalachian Mountains of North America. Another similarity is decreases in diameter growth of conifers on both continents, but these growth effects are more gradual in Europe and more synchronous in North America.

Table 1. Comparison of Symptoms of Decline in Forests of Europe and North America

Symptoms	Europe	North America
Growth-decreasing symptoms:		
1. Yellowing of foliage from the lower to the upper and from the inner to the outer portion of branches -- oldest tissues affected first.	Observed mainly in white fir and Norway spruce at high elevation.	Observed with white fir in the San Bernardino Mountains and recently in red spruce in New England and the southern Appalachians.
2. Dying back from the top of trees -- youngest tissues affected first.	Common in oak and ash, less common in birch and beech.	Conspicuous in red spruce, maple and oak declines; ash and birch diebacks.
3. Increased transparency of crowns due to gradual loss of leaves but with leaves retained to the very top of the trees.	Observed in Norway spruce, white fir, Scots pine, larch, beech, birch, oak, maple, ash, and alder.	Observed only in the littleleaf disease of shortleaf pine and in the beech-bark disease.
4. Losses of fine-root biomass and mycorrhizae (beneficial symbiosis between tree roots and soil fungi).	Common in white fir, Norway spruce and beech. Not studied in other species.	Observed mainly in red spruce and Fraser fir declines, birch dieback, and little leaf disease.
5. Synchronized decrease in diameter growth without other visible symptoms.	Not reported in Europe.	Observed in pitch pine and shortleaf pine.
6. Synchronized decrease in diameter growth with other visible symptoms leading to death.	Not reported in Europe.	Observed in red spruce and Fraser fir mainly at high elevation. Also ponderosa pine and Jeffrey pine.
7. Progressive decrease in diameter growth with other visible symptoms leading to death.	Studied mainly in Norway spruce, white fir and beech. Not studied in other species.	Observed in ash and birch diebacks, some maple and oak declines, sweetgum blight, littleleaf disease, and pole blight.
8. Death of herbaceous vegetation beneath some affected trees.	Observed in high elevation spruce and medium elevation beech forests.	Not observed in North America.

Table 1. (continued)

Symptoms	Europe	North America
Abnormal-growth symptoms:		
9. Active casting off (abscission) of leaves and shoots while still green.	Common in spruce, fir, and beech, ash larch, Scots pine, maple, and oak.	Reported only twice in North America, in loblolly pine and red spruce.
10. Change in relative length of long shoots and short shoots.	Common in beech and larch.	Reported only in the mycoplasma-induced "yellows" of ash.
11. Stork's nest crown formation in white fir	Common in white fir.	Not reported in North America.
12. Concentration of leaves in tufts or clumps at tips of branches.	Common in oak and ash.	Observed in nearly all declines of broad-leaved trees.
13. Change in size and shape of leaves.	Common in beech, occasionally in spruce, fir, birch, and oak, and Scots pine.	Common in white pine, littleleaf disease of shortleaf pine, and some maple and oak declines.
14. Excessive production of adventitious (out-of-place) shoots on branches.	Common in Norway spruce, White fir, and larch.	Observed recently for the first time in high altitude conifers. Common in maple and oak, ash, and birch.
15. Excessive production of seeds and cones.	Common in spruce, fir, beech, and birch; often observed several years in a row.	Observed in many stressed trees but mainly one year at a time.

Table 1. (continued)

General observations:

Many different species suddenly showing substantially similar symptoms.	Yes.	No.
Commercial forests showing extensive decline.	Yes.	Yes.
Soil relationships.	Trees affected on nutrient-rich and nutrient-poor soils, acid soils and basic soils.	Trees affected more on nutrient-poor and acid soils.
Elevation relationships.	Needle-bearing trees affected at all elevations.	Needle-bearing trees affected mainly at high elevation.

Symptom 3 has not been reported before 1979 affecting more than one species of trees.

Symptoms 8, 10, 14, and 15 have not been reported before 1980 affecting any tree species.

Symptom 9 has been reported only twice in North America and not before 1979 in central Europe.

4) Some of the most important differences in symptoms between North America and Europe include: a) the greater frequency of dying back from the top--youngest tissues affected first--in North America than in Europe; b) the greater frequency of abnormal-growth symptoms (symptoms 9-15 in Table 1) in Europe than in North America; and c) the substantial number of symptoms observed in Europe (symptoms 8, 9, 10, 11, and 14 in Table 1) that are reported only rarely or not at all in North America; and d) the greater frequency of decrease in growth without other visible symptoms of damage in North America than in Europe.

Concept of Multiple Causality of Declines in the Forests of Europe and North America

Regional declines of forests on both continents are believed to result from the combined action of several different competitional, biological, physical, and chemical stress factors that act simultaneously or sequentially to induce the symptoms of damage. One of the most widely accepted concepts of causality (Manion, 1981) holds that these three general types of stress factors act cumulatively as follows:

-- Predisposing competitional, physical, chemical, or biological factors which usually apply long-term chronic stresses.

-- Inducing or inciting biological, physical, or chemical factors which usually apply short-term acute stresses; and

-- Contributing competitional, biological, or physical stress factors which usually apply long-term stresses.

Although the concept of multiple causality has gained wide acceptance in both North America and in Europe, there is much less agreement among scientific specialists about which factors are predisposing, inducing or inciting, and contributing in any given decline of forests.

The competitional stress factors of importance to forests include competition for water, nutrients, and light are well as allelochemical interactions among individual both within and among species. Competition by hardwoods against conifers and among conifers in the same stand is often very keen, especially in even aged stands. Mortality induced by competition is an important feature of all planted and naturally regenerated forests. Only a few trees in the original stand will survive to maturity.

The biological stress factors of importance to forests include pathogenic and injurious fungi, insects, nematodes, bacteria, viruses, viroids, plasmids, mycoplasmas, and parasitic seed plants. The most important, by far, of these biotic stress factors in forests are fungi and insects.

The physical stress factors of importance to forests include wildfire and controlled burning of forests; extremes of heat and cold, especially rapid changes leading to sun scalding or frost injury; extremes of moisture supply, including both drought and flooding, as well as high winds and low humidity which contribute to moisture deficiency or to frost damage and winter desiccation.

The chemical stress factors of importance to forests include the following: toxic gases such as ozone and sulfur dioxide; excess nutrient substances especially nitrogen; toxic elements such as lead, cadmium, and fluorine; acidic substances such as sulfuric and nitric acids; acidifying substances such as ammonia vapor, and nitrate or ammonium sulfate aerosol; and growth-altering organic chemicals such as ethylene and aniline.

It is important to realize that the airborne chemicals of importance to forests include beneficial as well as injurious substances. The beneficial substances in the atmosphere include 16 chemical elements that are essential for growth of forest trees--carbon, hydrogen, oxygen, nitrogen, phosphorus, sulfur, potassium, calcium, magnesium, manganese, iron, copper, zinc, molbdenum, boron, and chlorine. All 16 of these essential elements can be taken up rapidly by forest trees directly through their foliage and green shoots as well as through their roots. Although attention is currently focused on injurious airborne chemicals, beneficial effects of airborne nutrients should always be recognized as a part of the normal growth and development processes in forests.

Possible Role of Airborne Chemicals in Declines of Forests

Clearly, not all regional declines of forests are caused by air pollution. Among the 18 regional declines listed earlier, airborne chemicals are considered to be a major causal factor in only four cases. These four are: a) the declines of Jeffrey and ponderosa pine in the San Bernardino Mountains of California; b) white pine decline in the eastern USA; c) Waldsterben, the general decline of softwood and hardwood forests in Europe; and d) the declines of red spruce and Fraser fir in the Appalachian Mountains from Maine to North Carolina in North America.

The quality of evidence that airborne chemicals are important in these forest declines varies greatly among these four cases. The strongest cases are the San Bernardino Mountain and white pine declines. In these cases, a) geographical gradients in damage are correlated with geographical gradients in ozone concentration (Miller et al. 1977, Skelly et al. 1983, Miller 1983); b) the major symptoms (yellowing and necrosis of foliage, decline in rate of growth, and death of trees) can be reproduced by exposure to ozone; and c) genetic variation in susceptibility and resistance to damage in the field is correlated with genetic variation in susceptibility and resistance to ozone in controlled exposures (Berry and Hepting 1963, Benoit et al. 1982).

In the case of Waldsterben, the evidence is less strong. Here, geographical gradients in damage are not well correlated with geographical gradients in concentration and/or deposition of any known air pollutants. But in at least one of the provinces of West Germany, Baden-Wurttemberg, the amount of damage to trees was greater on trees of greatest exposure to moving air masses. This was shown with regard to predominant wind direction, altitude, position within a stand (edge vs center), position within the canopy (dominant vs non-dominant trees), type of forest (pure softwood vs mixed softwood and hardwood forests), etc. (Institute for Forestry Experimentation and Research 1984). Also, no known biotic, physical, or soil-chemical factors were well correlated with damage. Finally, controlled exposure to ozone and to ozone plus acid mist has reproduced one of the symptoms (yellowing of spruce foliage) observed in the forest.

In the case of red spruce and Fraser fir declines, the evidence is weakest of all (Siccama et al. 1982; Johnson and Siccama 1983; Bruck 1984). Here, the amount of damage (decrease in diameter growth, loss of foliage and root biomass, and mortality of the trees) is greater at high than at low elevation. This is consistent with altitudinal gradients in concentration of ozone and other known pollutants, time of exposure to nutrient-rich and acidic cloud water, and accumulation of lead and other toxic metals. Neither controlled exposure tests nor genetic tests with resistant and susceptible genotypes have been done with red spruce or Fraser fir.

Airborne Chemicals of Greatest Probable Importance in the Current Declines of Forests

Except in the cases of ozone in the San Bernardino Mountain and white pine declines, present published evidence is not adequate to definitively link specific airborne chemicals to any particular decline of forests in either Europe or North America. On the basis of general knowledge of the responses of forests to stress, some circumstantial evidence, and a very few controlled-exposure tests, however, a consensus of informed judgement is developing that the airborne chemicals of greatest probable relevance to the current declines of forests include the following in approximate order of decreasing importance:

1) Ozone.

2) Total biologically available nitrogen compounds. This includes wet and dry deposition of all biologically available gaseous, aerosol, and dissolved or suspended forms of nitrate nitrogen (NO_3^- and HNO_3 vapor), ammonia nitrogen (NH_3), and ammonium nitrogen (NH_4^+).

3) Other phytotoxic gases, including nitrogen oxides (NO_x), sulfur dioxide (SO_2), fluorine (Fl), and both peroxacetyl nitrate (PAN), and peroxypropriony1 nitrate (PPN).

4) Toxic metals especially lead (Pb) and cadmium (Cd), and possibly also zinc (Zn) and copper (Cu).

5) Nutrient and acidity-determining cations and anions in wet and dry deposition ("acid deposition"), including potassium (K^+), sodium (Na^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), hydrogen (H^+), nitrate (NO_3^-), sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), and chloride (Cl^-).

6) Growth-altering organic chemicals such as ethylene and aniline.

Investigating the possible role of each of these six classes of airborne chemicals in the decline of forests in Europe and North America will require a substantial research effort extending over many years.

Rationale for the Ranking of Probable Airborne Chemical Stress Factors

Toxic substances are more likely to cause detrimental effects on plants than nutrient, acidic, or acidifying substances. Gases such as ozone have a greater potential for detrimental effects on plants than other physical forms of airborne chemicals (fine or coarse aerosol particles or substances dissolved or suspended in precipitation). This is true because gases can enter plants from the atmosphere directly through the stomata on leaves and green shoots. By contrast, aerosol particles and substances dissolved or suspended in precipitation can enter plants only after dissolution and/or diffusion through the protective surfaces of plants. These protective surfaces include the waxy cuticle of leaves and green shoots and the bark or other suberized tissues on the surface of twigs, branches, stems, and roots. Substances entering plants through roots would also have to survive the biological and physical adsorption and absorption hazards of percolation and/or diffusion through the pore structure of soils before entering plants.

Phytotoxic concentrations of ozone commonly occur in forests in Europe and North America. Toxic concentrations of nitrogen oxides, sulfur dioxide, peroxyacetyl nitrate, or peroxyproprionyl nitrate occur relatively infrequently in forests remote from point sources of pollutants.

Ozone accumulates in phytotoxic concentrations in all industrial regions of the world even at substantial distances from major sources of air pollutants. Ozone is a product of photochemical oxidation processes which occur whenever the precursor airborne chemicals [mainly oxides of nitrogen (NO_x) and volatile organic substances (VOC) such as unburned hydrocarbons, organic solvents, and other substances] are exposed to sunlight in air. For this reason, ozone is a regional rather than just a local hazard to normal growth and development of forests.

Ozone is known to cause severe injury and even death of certain forest trees. The best-known cases are white pine in much of eastern North America and ponderosa and Jeffrey pines in the San Bernardino Mountains of California.

Ozone acts synergistically with other pollutants. Ozone has been shown to cause more damage to certain agricultural crops in the United States and to spruce seedlings in West Germany when the exposure occurs in combination with other air pollutants such as sulfur and nitrogen oxides or simulated acid mist (Trajonis and Jacobson, personal communication; Prinz, personal communication).

Other toxic gases such as SO_2, NO, and NO_2 occur much less frequently in phytotoxic concentrations than ozone.

Although nitrogen is one of the most important nutrients required by forest trees for normal growth and development and is the element which most often is limiting to forest growth and productivity, it is also known to have certain detrimental effects on forest plants when deposited in greater than normal amounts and/or concentrations. These detrimental effects include the following: i) stimulation of increased growth leading to increased demand for all other essential nutrients and thus to deficiencies of other nutrient elements (Abrahamsen 1980); ii) increased susceptibility to frost and to winter desiccation due to delay in conversion of starches to sugars and/or in formation of protective cuticle on leaf surfaces (Tisdale and Nelson 1975, Friedland et al. 1985); iii) inhibition or necrosis of mycorrhizae--beneficial associations of fine feeder roots with certain soil fungi which assist in uptake of nutrients and water and afford protection against feeder-root pathogens of forest trees (Bjorkman 1949, Shafer et al. 1985); iv) predisposition to increased attack by foliage- and root-disease fungi (Huber 1980) and by insects (Hain 1984); v) changes in the relative amounts of shoot growth with respect to root growth (Aung 1974); and vi) alterations in patterns of nitrogen transformation in forest soils including nitrification, denitrification, and possibly biological fixation of nitrogen (Arthur Johnson, personal communication).

Certain toxic metals are known to accumulate in the organic matter and lesser vegetation on the floor of forests. This accumulation of toxic metals in forest floor materials is especially pronounced in high-elevation boreal forests (Johnson et al. 1982, Friedland et al. 1984b, 1984c) where other environmental conditions are also severe. However, current evidence suggests that available metal concentrations have rarely reached phytotoxic levels except near metal smelters and certain other point sources of these pollutants.

Simulated rain artificially acidified with sulfuric acid or mixtures of sulfuric and nitric acids have generally not been injurious to forest trees in controlled exposure experiments unless extraordinarily acidic solutions (les than pH 2.5) were used. This observation has been made repeatedly in experiments both in Europe and in North America. Acid deposition effects on soils and on mycorrhizae have yet to be evaluated fully.

Very few growth-altering organic compounds are known to be dispersed through the air in concentrations that would be injurious to plants. Nevertheless, the possibility exists that some among the myriad of commercially important volatile organic chemicals produced in industrial regions could prove to be injurious by inducing abnormal growth in forest trees. The observations of Cheesman et al. (1980) with regard to aniline and of Canadian scientists with regard to ethylene (Hutcninson, personal communication) are examples worthy of further attention.

The order of probable importance of these various airborne chemicals differs somewhat according to elevation. For example, atmospheric deposition of biologically available nitrogen compounds and toxic metals are more likely to be important in high-elevation than in low-elevation forests. Ozone, either alone or in combination with other toxic gases and drought, is the airborne chemical must likely to be important in low elevation forests.

Research efforts to determine the role of various airborne chemicals must not be separated from efforts to understand the normal functioning of forest ecosystems and their responses to competitional, physical climate, and biotic stress factors. Airborne chemicals do not act in isolation from the diverse competitional, physical, and biological stress factors that are a part of the dynamics of growth, development, productivity, disease, senescence, and death that are evident in all wild and managed forest ecosystems.

Implications for Management of Air Quality in Europe and North America

For some years or even decades now, the forests and surface waters of large parts of Europe and certain high-elevation, industrial, and urban locations in North America have been receiving much heavier loadings of nutrients, toxic, acidic, acidifying, and growth-altering chemicals than during the preindustrial period in which these ecosystems evolved. In some locations, essentially all the nutrients needed to grow some forests are now provided by deposition from atmospheric sources. Under these new circumstances, it should not be surprising that some beneficial and some detrimental changes in the health, productivity, and stability of forest ecosystems are being induced by these long-term regional, and even continent-wide changes in the chemical climate.

Sulfur dioxide is undoubtedly not the only airborne chemical injurious to aquatic and terrestrial ecosystems in Europe and North America. If ozone, biologically available nitrogen compounds, or toxic metals prove to be among the airborne chemicals that have significant detrimental effects on forests, it may be desirable to decrease regional emissions of nitrogen oxides, volatile organic compounds, and toxic metals, either simultaneously with, or independently of, possible future decreases in emissions of sulfur dioxide.

Significant decreases in emissions of sulfur dioxide, nitrogen oxides, and volatile organic compounds are likely to have significant and simultaneous beneficial effects on human health, visibility, materials damage, surface water quality, and both crop and forest productivity.

As a consequence of the long-distance transport of pollutants, their multiplicity, and the extensive mixing and complex chemical interactions among pollutants in the atmosphere, an integrated (multiple pollutant and regional) program for management of air quality would have several advantages over the present single-pollutant and state-by-state or province-by province methods of planning both in Europe and North America.

REFERENCES

Abrahamsen, G. 1980a. Acid precipitation, plant nutrients, and forest growth, pp. 58-63. In Ecological Impact of Acid Precipitation. D. Drabløs and A. Tollan (eds.). Proc. of an International Conference, Sandefjord, Norway. SNSF Project. Oslo-Å, Norway.

Abrahamsen, G. 1980b. Effects of acid precipitation on soil and forest. 4. Leaching of plant nutrients, p. 196. In Ecological Impact of Acid Precipitation. D. Drabløs and A. Tollan (eds.). Proc. of an International Conference, Sandefjord, Norway. SNSF Project. Oslo-Ås, Norway.

Aung, L.H. 1974. Root-shoot relationships, pp. 29-62. In The Plant Root and its Environment. E.W. Carson (ed.). University Press of Virginia, Charlottesville.

Beamish, R.J. and H.H. Harvey. 1972. Acidification of the LaCloche Mountain Lakes, Ontario, and resulting fish mortalities. J. Fish. Res. Bd. of Can. 29:1131-1143.

Berry, C.R. and G.H. Hepting. 1964. Injury to eastern white pine by unidentified atmospheric constituents. For. Sci. 10:2-12.

Bjorkman, E. 1949. Ecological significance of ectrotrophic mycorrhizal associations of forest trees. Svenst Botaniska Tidskrift 42. 223 pp.

Bruck, R.I. 1984. Decline of montane boreal ecosystems in central Europe and the Southern Appalachian Mountains. TAPPI Proceedings 1984:159-163.

Cheesman, J., T.O. Perry, and W.W. Heck. 1980. Identification of aniline as an air pollutant through biological assay with loblolly pine. Env. Poll. (Series A) 21:9-22.

Davis, D.D. and F.A. Wood. 1972. The relative susceptibility of eighteen coniferous species to ozone. Phytopathology 62:14-19.

Eriksson, E. 1952. Composition of Atmospheric Precipitation. I. Nitrogen Compounds. Tellus 4:215-231. II. Sulfur, Chloride, Iodine Compounds. Bibliography. Tellus 4:280-303.

Eriksson, E. 1954. Report of an Informal Conference in Atmospheric chemistry Held at the Meteorological Institute, University of Stockholm, May 24-26, 1954. Tellus 6:302-307.

Eriksson, E. 1959. The Yearly Circulation of Chloride and Sulfur in Nature: Meteorological, Geochemical, and Pedological Implications. Part I. Tellus 11:375-403.

Eriksson, E. 1960. The Yearly Circulation of Chloride and Sulfur in Nature: Meteorological, Geochemical, and Pedological Implications. Part II. Tellus 12:63-109.

Friedland, A.J., R.A. Gregory, L. Karenlampi, and A.H. Johnson. 1984a. Winter damage to foliage as a factor in red spruce decline. Can. J. For. Res. 14:963-965.

Friedland, A.J., A.H. Johnson, and T.G. Siccama. 1984b. Trace metal content of the forest floor in the Green Mountains of Vermont: Spatial and temporal patterns. Water Air Soil Pollut. 21:161-170.

Friedland, A.J., A.H. Johnson, T.G. Siccama, and D.L. Lader. 1984c. Trace metal profiles in the forest floor of New England. Soil Sci. Soc. Am. J. 48:422-425.

Gorham, E. 1955. On the Acidity and Salinity of Rain. Geochim. Cosmochim. Acta 7:231-239.

Gorham, E. 1957. The Ionic Composition of Snow Lowland Lake Water from Cheshire, England. Limnol. and Oceanogr. 2:22-27.

Gorham, E. 1958. The Influence and Importance of Daily Weather Conditions in the Supply of Chloride, Sulphate, and Other Ions to Fresh Waters from Atmospheric Precipitation. Phil. Trans. Royal Soc. London (Series B) 247:147-178.

Gorham, E. 1961. Factors Influencing Supply of Major Ions to Inland Waters, with Special Reference to the Atmosphere. Geol. Soc. Amer. Bull. 72:795-840.

Gorham, E. and A.G. Gordon. 1960. The Influence of Smelter Fumes Upon the Chemical Composition of Lake Waters Near Sudbury, Ontario, and Upon the Surrounding Vegetation. Can. J. Bot. 38:477-487.

Hain, F. 1985. The role of atmospheric deposition in the latitudinal variation of Fraser fir mortality caused by the Balsam Woolly Adelgid. Zeitschrift für angewandte Entomologie. In press.

Hepting, G.H. 1963. Climate and forest declines. Annual Rev. Phytopath. 1:31-50.

Huber, D.M. 1980. The role of mineral nutrition in defense. In Plant Disease: An Advanced Treatise. Vol. V. How Plants Defend Themselves. G. Horsfall and E.B. Cowling, eds., Academic Press, New York. 5:381-406.

Hultberg, H. and J. Stenson. 1970. Effects of Acidification on the Fish of Two Small Lakes in Bohuslan, Southwestern Sweden. Flora Fauna 1:11.

Institute for Forestry Experimentation and Research. 1984. Major Results of the Data Analysis of the Extensive Terrestrial Inventory of Forest Damage in Baden-Wurttemberg in 1983 using Pine and Spruce Trees as Bioindicators. (Translated by the Congressional Research Service, the Library of Congress, Washington, DC.) Institute for Forestry Experimentation and Research. Baden-Wurttemberg, FRG.

Jensen, K.W. and E. Snekvik. 1972. Low pH Levels Wipe Out Salmon and Trout Populations in Southernmost Norway. Ambio 1:223-225.

Johnson, A.H. and T.G. Siccama. 1983. Acid deposition and forest decline. Environ. Sci. Techn. 17:294-306.

Johnson, A.H., T.G. Siccama, and A.J. Friedland. 1982. Spatial and temporal patterns of lead accumulation in the forest floor in the northeastern United States. J. Environ. Qual. 11:577-580.

Junge, G.E. and R. Werby. 1958. The Concentration of Chloride, Sodium, Potassium, Calcium, and Sulfate in Rain Water Over the United States. J. Meteorol. 15:417-425.

Manion, P.D. 1981. Tree Disease Concepts. Prentice-Hall, Inc. Englewood Cliffs, NJ. 399 pp.

Miller, P.R. 1983. Ozone effects in the San Bernardino National Forest, pp. 161. In Air Pollution and the Productivity of the Forest. D.D. Davis, A.A. Millen and L. Dochinger (eds.).

Miller, P.R. 1973. Oxidant-induced community change in a mixed conifer forest. In Air Pollution Damage to Vegetation. J.A. Naegela, ed. p. 101-117. Adv. in Chem. Series 122. Amer. Cham. Soc., Washington, DC.

Miller, P.R., M.H. McCutchan, and H.P. Millegan. 1972. Oxidant air pollution in the central valley, Sierra Nevada foothills, and Mineral King Valley of California. Atmos. Environ. 6:623-633.

Miller, P.R. and A.A. Millecan. 1971. Extent of oxidant air pollution damage to some pines and other conifers in California. Plant Dis. Reptr. 55:555-559.

Miller, P.R., J.R. Parmeter, Jr., O.C. Taylor, and E.A. Cardiff. 1963. Ozone injury to the foliage of Pinus ponderosa. Phytopathology 53:1072-1076.

Odén, S. 1967. Dagens Nyheter. October 24, 1967.

Odén, S. 1968. The Acidification of Air and Precipitation and its Consequences in the Natural Environment. Ecology Committee Bulletin No. 1. Swedish National Science Research Council, Stockholm. Translation Consultants, Ltd., Arlington, Virginia. 117 pp.

Odén, S. and T. Ahl. 1970. Forsurningen av skandenaviska vatten. (The Acidification of Scandinavian Lakes and Rivers.) Ymer, Arsbok:103-122.

Jensen, K.W. and E. Snekvik. 1972. Low pH Levels Wipe Out Salmon and Trout Populations in Southernmost Norway. Abmio 1:223-225.

Johnson, A.H. and T.G. Siccama. 1983. Acid deposition and forest decline. Environ. Sci. Techn. 17:294-306.

National Academy of Sciences. 1977. Ozone and other photochemical oxidants. NAS, Washington, DC. 789 pp.

Schutt, P. and E.B. Cowling. 1985. Waldsterben--A general decline of forests in Central Europe: Symptoms, development, and possible causes of a beginning breakdown of forest ecosystems. Plant Disease 69: (in press).

Shafer, S.R., L.F. Grand, R.I. Bruck, and A.S. Heagle. 1985. Formation of ectomycorrhizae on Pinus taeda seedlings exposed to simulated acid rain. Can. J. For. Res. 15:66-71.

Siccama, T.G., M. Bliss and H.W. Vogelmann. 1982. Decline of red spruce in the Green Mountains of Vermont. Bull. Torrey Bot. Club 109:163-168.

Skelly, J.M., Y.S. Yang, B.I. Chevone, S.J. Long, J.E. Nellessen and W.E. Winner. 1983. Ozone concentrations and their influence on forest species in the Blue Ridge Mountains of Virginia, pp. 143-159. In Air Pollution and the Productivity of the Forest. D.D. Davis, A.A. Millen and L. Dochinger (eds.). Izaak Walton League and Pennsylvania State University.

Smith, R.A. 1872. Air and Rain: The Beginnings of a Chemical Climatology. Longmans, Green, London. 600 pp.

Tisdale, S.L. and W.L. Nelson. 1975.. Soil Fertility and Fertilizers. MacMillan Publ. New York. 694 pp.

ADDRESS ON CURRENT LEGISLATIVE/REGULATORY SITUATION

by: Joseph A. Cannon
Pillsbury, Madison and Sutro
Washington, DC 20006

No written presentation furnished.

THE ROLE OF FGD IN SO_2 REDUCTION STRATEGIES FOR COAL-FIRED POWER PLANTS

By

E.S. Rubin, M. Cushey, R.J. Marnicio, C.N. Bloyd and J.F. Skea
Carnegie-Mellon University
Pittsburgh, Pennsylvania

Abstract

A newly developed computer model for detailed analysis of SO_2 control strategies and costs at the unit, state and regional levels is described. Illustrative results are presented in which a broad range of parameters affecting FGD retrofits at existing coal-fired power plants are examined for an eight-state region of the midwest, using site-specific plant and fuel characteristics. The future cost and capacity of FGD retrofit systems is seen to depend strongly on SO_2 reduction requirements. For the highest levels of control, wet limestone scrubbing in conjunction with physical coal cleaning often provided the most economical means of compliance, particularly if only "local" coals were used. The future availability of dry SO_2 removal processes (lime spray dryer and LIMB) is seen to have a potentially significant influence on the choice of SO_2 control technology, should emission reductions of 50% or more become required in the next decade. The potential effects of plant life extension programs on the use of conventional and advanced FGD systems also is significant. The way in which overall SO_2 emission reductions are allocated to individual sources, and the degree to which utility coal choices are constrained, also have a pronounced effect on control technology selection and cost.

INTRODUCTION

In the past decade the use of flue gas desulfurization (FGD) systems for air pollution control has increased dramatically. Ten years ago, less than 4000 MW of FGD capacity was installed on U.S. power plants, versus 50,000 MW today. This change was due to passage of the Clean Air Act Amendments of 1970 and the subsequent promulgation of federal New Source Performance Standards (NSPS). For coal-fired power plants, the original NSPS requirements adopted in 1971 could be met either by installing an FGD system or by using a sufficiently low sulfur fuel. In 1979, this was changed to require 70-90% sulfur removal on all new coal-fired facilities. Units constructed prior to 1971 have not yet been affected as significantly as new sources. While a number of FGD systems have been retrofitted to comply with State Implementation Plan (SIP) emission requirements, most existing facilities either have been unaffected or have been able to comply with SIP requirements by converting to lower sulfur fuels.

All this may change significantly if new "acid rain" controls are enacted by Congress. Proposals introduced in recent years have called for SO_2 reductions in the 31 eastern states of 8 to 12 million tons/year below total 1980 levels, to be achieved over the next decade. Much of this would come from existing coal-fired power plants, which could be required to reduce emissions by up to 90% or more under some of the formulas proposed [1]. Thus, over the next decade the role of FGD as a sulfur abatement strategy again could increase dramatically.

In this paper we examine a number of technical and economic factors that will affect the extent to which FGD may be implemented at existing coal-fired power plants if new emission reductions are required. We do not analyze any particular legislative proposals or policies. Rather, we focus on the role of alternative sulfur removal technologies that are currently available or under development, and explore their potential use and cost under a variety of scenarios. To do this we use a new simulation model of the electric utility sector which accounts for many of the site-specific factors affecting control strategy selection. First, we briefly describe this model, then we present results of an application to several midwestern states.

OVERVIEW OF THE MODELING FRAMEWORK

Over the past several years the U.S. Environmental Protection Agency (EPA) has supported the development of the Advanced Utility Simulation Model (AUSM), a preliminary version of which has recently been completed [2]. A model analogous to the state-level AUSM also has been developed at Carnegie-Mellon University to focus specifically on the technical and economic analysis of control strategy selection for existing coal-fired power plants over the next 10 to 15 years. We call this the Utility Control Strategy (UCS) model. It contains refined versions of the same pollution control components developed for the AUSM, together with other models of coal supply and transport, electricity demand, power plant dispatch and system impacts.[1] The model may be exercised on a regional or state level basis in the framework of an annually recursive loop for a period of up to 20 years beginning in 1980. Pollution control costs are analyzed at the individual unit level using a detailed plant inventory which contains information on the size, type, performance, age, fuel use, pollution control equipment and environmental regulations of each generating unit in the country. The following paragraphs outline the treatment of SO_2 control options, which is the focus of this paper. Other details of the model may be found elsewhere [3].

---

[1] Assumptions and results of the UCS model therefore may differ from the AUSM, which is being further modified and developed by EPA.

The Pollution Control Module

The function of the pollution control module is to select appropriate coals and pollution control equipment for both new and existing coal-fired plants. Information on alternative coals is generated by a coal supply module which determines the coals with the lowest delivered energy cost to power plants in each demand region.[2] This is done for each of three coal ranks (bituminous, sub-bituminous and lignite), and for each of 11 ranges of sulfur content (specified in lbs SO_2/MBtu). The coal supply module also can be constrained to restrict the choice of coals that are available to power plants.

For existing plants that must reduce their SO_2 emissions, the pollution control module considers the alternatives of coal switching, coal blending, scrubbing,[3] combinations of scrubbing and coal switching, and early retirement. Physical coal cleaning also is included as a control option, with coals washed for sulfur removal allowed to compete with unwashed coals on a delivered energy cost basis for each sulfur category. In addition to considering switching to an alternative coal, the model also creates blended coals for units which must meet a source-specific emission standard. This is done by mixing the current coal with lower sulfur alternative coals in proportions which exactly meet the applicable standard. For plants already using a blend of coals, the model also seeks compliance by adjusting the ratio of the coals presently in use. Finally, the installation of an FGD system is considered for the current coal and the 11 alternative coals of both higher and lower sulfur content. The SO_2 removal options currently included in the model are a conventional wet limestone system, a lime spray dryer system, and a limestone injection multistage burner (LIMB) system.

Control options for particulate and NO_x emissions also are part of the model. Alternatives for NO_x control include overfire air, low-NO_x burners or a combination of these. LIMB also is assumed to achieve NO_x as well as SO_2 reductions. For particulate control, models of electrostatic precipitators (hot-side and cold-side) and a fabric filter (baghouse) collector are included. For an existing plant, the model does not allow particulate emissions to increase as a result of complying with an SO_2 regulation. Thus, an upgrade requirement (and associated cost) is imposed wherever necessary, most commonly when switching to a lower sulfur coal (because of increased fly ash resistivity). For plants retrofitting dry FGD or LIMB, the feasibility and cost of using an existing ESP to handle the higher particulate loadings of lower sulfur materials is not yet well defined. The default assumption is that a new fabric filter collector is required. Alternatively, however, parameter values for additional capital ($/kW) and annual (mills/kWh) costs for upgrading an existing ESP can be specified for each technology to reflect less conservative assumptions.

For the conventional case of unit-specific emission standards, the control strategy selected by the model is the combination of SO_2, particulate and NO_x control options which results in the lowest levelized cost over the remaining life of the facility. This cost calculation takes into consideration the delivered cost of fuel, plus the additional capital and operating costs of all air pollution control and solid waste disposal systems. It also reflects the expected rates of inflation, real cost escalation (capital and variable), and return on debt and equity. Control strategy costs are compared in constant dollars on an after-tax basis for user-specified values of federal and state income taxes, insurance, property taxes, investment tax credits, and depreciation schedules.

---

[2] The UCS model has 35 coal supply regions and 66 demand nodes, with up to four demand regions per state depending upon the predominant transport modes.

[3] We use the words "scrubbing" and "FGD" rather loosely here to include any retrofit control technology which removes sulfur during or after combustion.

Once control strategy decisions are made and implemented the "actual" values of plant use, coal consumption, emissions and costs can be determined on a year-by-year basis by "dispatching" all available capacity (including coal, nuclear, oil, gas and other facilities) to meet a given electricity demand. In this paper, however, our analysis of control strategy selection is limited to an *a priori* analysis of alternative options based on expected values of future plant utilization.

SO_2 CONTROL TECHNOLOGY MODELS

References 4 and 5 present detailed descriptions of the SO_2 control technology performance and cost models. These were developed for new plants and are applied to existing facilities through the use of a "retrofit factor." The nature of these models is briefly summarized below.

Wet Limestone Scrubbing

Among competing FGD systems, wet limestone processes are the most prevalent now in use, and are incorporated as the nominal FGD option for coal-fired power plants. The analytical models for wet FGD performance and cost were derived from results of the detailed cost estimation model developed by the Tennessee Valley Authority (TVA) [6]. Algorithms developed by Molburg and Rubin [7] were refined using multiple regression analyses of results from approximately 600 runs of the TVA model over a wide range of power plant sizes, heat rates, coal characteristics, SO_2 removal requirements and scrubber design configurations (including variations in reagent stoichiometry, liquid-to-gas ratio, and numbers of spare and operating trains). Separate algorithms were developed for capital cost and operating cost for each of three plant areas: reagent handling and preparation; scrubber trains; and solid waste disposal. Excellent statistical fits to the TVA results were achieved in every case (typical R^2 values of 0.98 or greater) [4].

Using these models, FGD costs are estimated on the basis of the flue gas flow rate, reagent requirement and sulfur removal requirement of an individual facility. The nominal system design assumes use of a spray tower absorber with forced oxidation, landfill disposal of wastes, and one spare scrubber train for each four operating trains. It also assumes that partial scrubbing (at 90% SO_2 removal) is used wherever permissible and economical. Another option allows upgrading the performance of an existing scrubber through the addition of an organic additive.

Lime Spray Dryer

Dry FGD systems employing a lime spray dryer and baghouse collector are emerging as the preferred option for many new coal-fired plants using western low sulfur coal. While this technology has not yet been commercially used as a retrofit option for plants burning medium or high sulfur eastern coals, it is included in the overall modeling framework as a potential alternative to wet FGD. Development of the dry FGD model was based on a number of recent studies by TVA and others of new plants employing high sulfur as well as low sulfur coals [4]. The model system is assumed to operate at a nominal SO_2 removal efficiency of 70% for the spray dryer-baghouse combination, with efficiencies up to 90% achievable at higher stoichiometries. Since reliable specification of molar stoichiometry over a full range of utility coals and performance requirements is not yet available, data from pilot plants and small scale applications currently provide the principal basis for estimating performance for coals with higher sulfur content and lower alkalinity than those used in current commercial applications. The relationship used in the UCS model specifies molar stoichiometric as an exponential function of SO_2 removal efficiency with a value of 1.1 moles Ca/mole S at a removal efficiency of 70%.[4] Warm gas bypass is assumed to achieve a 160°F gas temperature downstream of the dryer.

Capital and operating cost models again were developed for each of three major components (materials handling, scrubber system and solid waste disposal) based on regression analysis of results from detailed studies [4]. Dry waste is assumed to be disposed of in a landfill, with the mass of waste dependent upon reagent stoichiometry, extent of oxidation, and the masses of sulfur and fly ash removed. The performance and cost models for a fabric filter collector used in conjunction with the spray dryer assume a default air-to-cloth ratio of 2.0. Alternatively, increased capital and operating costs may be specified for upgrading an existing ESP, as noted earlier.

Furnace Limestone Injection

The simultaneous removal of sulfur and nitrogen oxides through furnace injection of limestone or other sorbents is a third retrofit option included in the model. Since LIMB is still a developing technology which remains to be commercially demonstrated, its cost and performance are modeled in a simple fashion to allow a range of hypotheses to be tested easily. The default parameters assume that LIMB achieves 50% sulfur removal at a stoichiometry of 3.0 moles Ca/mol S in retrofit applications. Costs are modeled separately for reagent handling/preparation, boiler modification, particulate removal, and waste disposal systems. Regression models for materials handling and preparation costs are similar to those for a wet limestone FGD system, though costs are lower because of some differences in equipment. Boiler modification costs are defined simply as a cost per kilowatt of installed capacity, with a default value of $13/kW. Waste disposal costs employ the same algorithms developed for spray dryer systems assuming landfill disposal. Particulate control costs nominally assume a new fabric filter collector, though provision again is made to utilize an existing ESP with user-specified costs for upgrading the system.

Physical Coal Cleaning

Technical options for removing sulfur from coal prior to combustion are included as part of the coal supply model. Models for estimating the cost of coal washing were derived by "processing" each of the nearly 800 coals in the U.S. Bureau of Mines washability data base through a coal preparation plant computer model that employs coal-specific washability data for each of four model plants of increasing complexity. Multivariate regression models yielding washed coal properties and cost as a function of sulfur removal level then were developed for each of 18 geographical regions to which coals were assigned [5]. By allowing washed coals to compete with unwashed coals in any sulfur category, coal cleaning may be used in conjunction with FGD to minimize overall power generation costs in the model [8]. An option also exists to employ mandatory coal washing provided appropriate criteria are specified.

---

[4] Note that the conventional definitions of molar stoichiometry differ for wet and dry removal processes.

RESULTS FOR A SINGLE PLANT

Table 1 lists the key economic and financial assumptions used in this paper as a "base case." Table 2 shows the results of applying the analytical models of wet FGD, dry FGD and LIMB to a single coal-fired unit. In this example, the plant is assumed to reduce its emissions beginning in 1995 using its current coal. Nominal SO_2 removal efficiencies of 90%, 70% and 50% are assumed for wet FGD, dry FGD and LIMB, respectively, with retrofit capital costs for all pollution control equipment assumed to be 30% higher than for a new plant. The levelized costs per ton of SO_2 removed represent the expected increased cost of SO_2 removal, particulate control and solid waste disposal (in constant 1984 dollars) over the plant's remaining life. These costs are in general agreement with other recent cost estimates for these technologies [9,10] when expressed on a similar basis. In particular, the reader should note that the use of "current dollars" for reporting levelized costs gives results that are significantly higher than the "constant dollars" costs used throughout this paper. Table 3 illustrates this point.

STATE LEVEL ANALYSIS

The unit level analysis is the building block for more comprehensive analyses of states and regions. The state level was chosen for consideration since it is the level at which air pollution control policy is implemented for existing sources, as well as the level at which utilities rates are regulated. Historically, SO_2 emission reductions have been achieved largely through uniform local or statewide emission caps applicable to each unit (typically expressed as allowable lbs SO_2/MBtu). For this case, the UCS model seeks the lowest cost compliance option for each unit.[5]

An alternative to this approach is a "least cost" emission reduction strategy for a state as a whole. By ranking alternative strategies for individual plants according to their cost effectiveness of control (measured in $/ton of SO_2 removed), a "marginal cost of control" curve can be developed for the entire set of plants in a state. Figure 1 shows an example of this, indicating the statewide average as well as the marginal cost of control for increasing SO_2 abatement levels. For any specified level of total emissions reduction, the corresponding point on the marginal cost curve specifies the set of plant-specific abatement strategies which minimizes overall cost.

Table 4 shows UCS model results for a case analyzing a target 887 ktpy (80%) reduction for the state of Pennsylvania in 1995. Here, FGD retrofits are selected for 74% of the eligible capacity, partially in conjunction with coal switching. (Note that in this example all costs are reported in constant 1980 dollars.) In the examples which follow analyses of this type are used to examine the role of FGD in the larger context of an eight state region of the midwestern United States.

---

[5] This follows a procedure similar to the one outlined in Table 2, except that an incremental fuel cost also becomes part of the annual O&M expense. Depending on the value of the emission cap and the number of FGD options assumed to be available, anywhere from 12 to approximately 100 systems (i.e., different combinations of coals, SO_2 and TSP removal devices) may be evaluated for each unit.

Table 1
Economic and Financial Assumptions for Base Case Scenarios[a]

Model Parameter	Nominal Value
General inflation rate	6%
Return on debt	12%
Return on equity	14%
Debt/equity ratio	52.6/47.4
Federal tax rate	46%
State tax rate	4%
Ad valorem charges	4.5%
Investment tax credit rate	11.75%
Tax credit eligibility	100%
Tax life (retrofits)	5 Years
Capital cost escalation rate (real)	0.0
Retrofit cost factors	1.30
Limestone cost (1984 $)	$14/ton
Lime cost (1984 $)	$63/ton
In-plant energy cost (1984 $)	60 mills/kWh
Variable cost escalation rate (real)	0.0
Energy cost escalation rate (real)	0.0
FGD construction time	3 Years
FGD expenditure schedule (%/yr)	25/50/25
Coal price escalation rates (real %/yr)[b]	1.5/0.75/0.00/0.0
Transportation price escalation rate (real)	1.5%/yr

[a] A complete list of all model parameters appears in Ref [4].

[b] Applies to mine mouth prices of UCS model coals with sulfur content (lbs SO_2/MBtu) in the ranges: $\leq$ 1.2/1.2-1.8/1.8-3.0/$\geq$ 3.0.

Table 2
Estimated 1995 Retrofit Costs for One Coal-Fired Plant Using Its Current Coal (Constant 1984 Dollars)[a]

Cost Component	Wet FGD[b]	Dry FGD[c]	LIMB[d]
Capital Costs ($/kW)			
SO_2 Removal	193	135	41
TSP Removal[e]	0	60	70
Solid Waste[f]	44	40	37
Total	237	235	148
Annual O&M Costs ($/kW-yr)			
Control Systems[g]	17.0	14.7	7.5
Utilities	12.3	4.8	2.3
Total	29.3	19.5	9.8
Total Levelized Cost			
Rev. Reqm't (mills/kWh)	10.4	8.6	4.9
SO_2 Removal ($/ton SO_2)	730	789	620

[a] Unit characteristics; 614 MW (net); 9382 Btu/kWh; 63.5% capacity factor; 19 year lifetime. Coal properties: 11,487 Btu/lb; 2.0% sulfur; 19.7% ash.

[b] Wet limestone system with 90% sulfur removal.

[c] Lime spray dryer system with 70% sulfur removal.

[d] Furnace limestone injection system with 50% sulfur removal.

[e] Assumes a new fabric filter collector with dry FGD or LIMB.

[f] Assumes co-disposal of fly ash and FGD wastes.

[g] Includes all fixed and variable O&M costs except utilities.

Table 3
Effect of Cost Reporting Method on Levelized Costs of Control: Constant vs. Current Dollars for the Same Real Discount Rate[a]

Case	Levelized Capital Cost ($M)[b]	Levelized O&M Cost ($M)[b]	Levelized Revenue Reqm't ($M)	SO_2 Removal Cost ($/ton removed)
Case I: Constant Dollars				
3.7% discount rate plus 0% inflation	7.1	10.0	17.1	342
Case II: Current Dollars w/				
10.0% discount rate plus 6.1% inflation	12.7	19.1	31.8	636
Case III: Current Dollars w/				
12.5% discount rate plus 8.5% inflation	15.3	23.1	38.4	768

[a] Based on an assumed capital cost of $100 million, annual O&M cost of $10 million, and SO_2 removal of 50,000 tons/yr, with zero real cost escalation. All cases have a real discount rate of 3.7%.

[b] Based on factors for a 30-year book life tabulated by EPRI [11]. The real discount rate for these cases is $\frac{d - i}{1 + i}$,

where d is the nominal discount rate and i is the inflation rate.

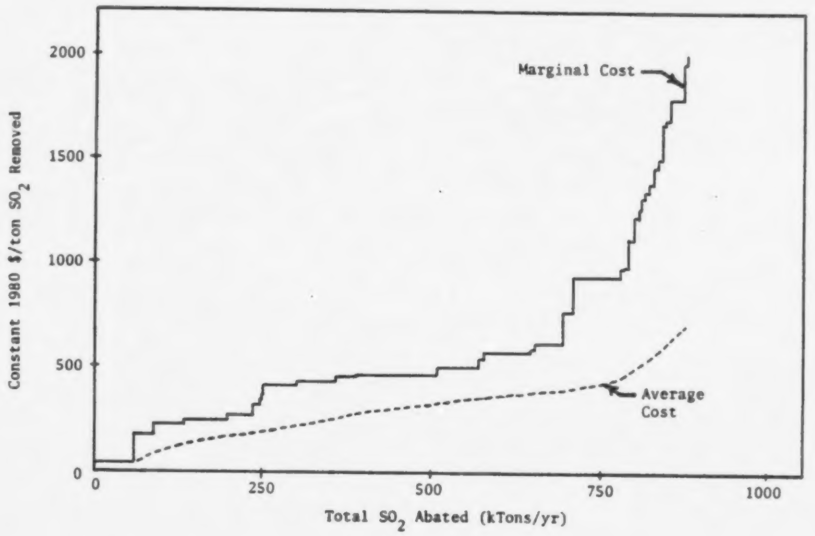


Figure 1
Example of Marginal and Average SO_2 Abatement Costs for a Single State

Table 4
Sample UCS Model Results for A Statewide Least Cost Strategy
(All Costs are in Constant 1980 Dollars)

Report on Abatement Strategies and Costs at Retrofit Plants - PENNSYLVANIA 1992

Least Cost Strategy: Target Reduction - 887 ktons Marginal Abatement Cost - $1433 /ton SO2

Strategy Chosen	SCRUBBING	SWITCHING	BLENDING	SCRUB/SWITCH	RETIRAL	UPGRADE	COMPLYING	TOTAL
Cap inc byp (GW)	2.78	3.49	0.00	7.03	0.00	0.00	0.00	13.30
% of Total	20.9	26.2	0.0	52.9	0.0	0.0	0.0	100.0
Generation (TWh)	14.59	13.38	0.00	39.42	0.00	0.00	0.00	67.39
SO2 Abated (kton)	211.4	88.4	0.0	586.0	0.0	0.0	0.0	885.7
Cap Costs ($M)	551.37	28.31	0.00	1297.17	0.00	0.00	0.00	1876.84
SO2 Control	455.69	0.00	0.00	1098.57	0.00	0.00	0.00	1554.26
($/kw)	163.9	0.0	0.0	156.2	0.0	0.0	0.0	116.9
TSP Control	0.00	22.21	0.00	0.00	0.00	0.00	0.00	22.21
($/kw)	0.0	6.4	0.0	0.0	0.0	0.0	0.0	1.7
NOX Control	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
($/kw)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Solid Waste	95.67	6.09	0.00	198.60	0.00	0.00	0.00	300.36
($/kw)	34.4	1.7	0.0	28.2	0.0	0.0	0.0	22.6
O & M Costs ($M)	64.96	20.58	0.00	158.52	0.00	0.00	0.00	244.07
Fuel	0.00	20.47	0.00	-8.60	0.00	0.00	0.00	11.87
Poll Control	38.17	0.04	0.00	95.04	0.00	0.00	0.00	133.24
Cap Penalty	26.80	0.07	0.00	72.08	0.00	0.00	0.00	98.95
Level Cost ($M)	138.20	28.06	0.00	311.08	0.00	0.00	0.00	477.33
mills/kWh	9.47	2.10	0.00	7.89	0.00	0.00	0.00	7.08
$/ton SO2 abated	653.9	317.5	0.0	530.9	0.0	0.0	0.0	538.9
Cpcty Scrubbed (GW)	2.78	0.00	0.00	7.03	0.00	0.00	0.00	9.81
% of Total	28.3	0.0	0.0	71.7	0.0	0.0	0.0	100.0
Tot Cst ($/kWscrub)	198.3	0.0	0.0	184.5	0.0	0.0	0.0	191.3
% of Int SO2	19.3	8.1	0.0	53.6	0.0	0.0	0.0	81.0

Final SO2 Emissions 208.3ktons Initial SO2 Emissions 1094.0ktons

ANALYSIS OF A MULTI-STATE REGION

A number of previous studies have focused on the 31-state region of the eastern U.S., which has been targeted for SO_2 emission reductions under a number of acid rain control bills. These studies generally have been concerned with the overall cost of SO_2 abatement for specific legislative proposals, and with the effects of such proposals on regional coal markets. In this paper we take a more careful and comprehensive look at some of the technical and economic factors affecting the selection of FGD systems in the event new emission reduction requirements are imposed on existing sources. We also explore the sensitivity of these results to a wide number of factors not heretofore analyzed systematically, including the impact of potential technical advances from increased research and development.

Our analysis focuses on the eight midwestern states whose utility SO_2 emissions currently are the largest in the country. Table 5 shows several summary statistics for these states. In 1980, total coal-fired power plant capacity was 116,000 MW, of which approximately 10,000 MW (8.4%) was equipped with FGD. Average SO_2 emissions for coal-fired plants in these states ranged from 2.8 lbs/MBtu in Pennsylvania to 4.8 lb/MBtu in Missouri. Total 1980 SO_2 emissions amounted to 10.5 Mtpy, or approximately 70% of all utility SO_2 emissions in the 31 eastern states.

Scenario Parameters and Assumptions

To examine the future role of FGD in this region an extensive set of model runs was undertaken in which some 15 parameters were varied alone and in combination. Clearly, the principal determinant of FGD use at existing facilities will be the required level of emissions reduction. We examined SO_2 reduction requirements of 50%, 65% and 80% of uncontrolled emissions from the 101 GW of capacity not already equipped with FGD in 1980, and not scheduled to retire before the assumed compliance year of 1995.[6]

Two related factors examined were constraints on utility coal use, and flexibility for cost minimization. Constraints on coal use were modeled as a requirement to use only "local" coals produced within the state, in contrast to the unconstrained situation where any suitable coal could be considered.[7] A further restriction considered only the use of current coals at each plant.

The flexibility constraint concerned the way in which emission reduction requirements are allocated to individual sources. Three cases were considered. The nominal case reflected the current situation of uniform standards applied to individual units in a state. In these scenarios, allowable emissions from each unit were restricted to the more stringent of its current SIP standard or a uniform statewide cap chosen to achieve the desired overall reduction. The value of this cap thus differed from state to state for each reduction level considered. A second case considered statewide least cost solutions, as described earlier. This assumes that appropriate mechanisms are available to implement the

---

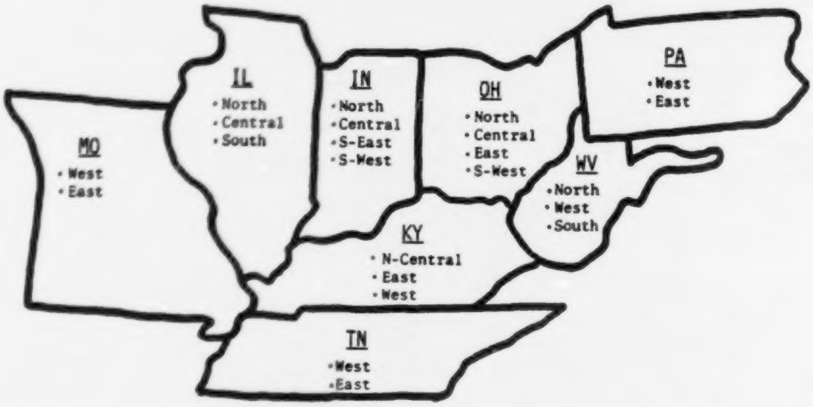
[6] These reductions levels roughly approximate those that would be required by recent congressional proposals calling for 31-state emission reductions of 8, 10, and 12 Mtpy. Certain midwestern states, however, would be affected more severely by specific proposals.

[7] Suitable coals were defined here as being of the same rank (bituminous, sub-bituminous or lignite) as the current coal in use. In addition, cyclone fired boilers were prohibited from switching to coals with less than 2% sulfur to ensure suitable ash fusion temperatures.

Table 5

UCS Model Demand Regions and 1980 Characteristics of Coal-Fired Power Plants in the Eight-State Study Region

UCS Model Coal Demand Regions


IL
• North
• Central
• South
IN
• North
• Central
• S-East
• S-West
OH
• North
• Central
• East
• S-West
PA
• West
• East
MO
• West
• East
WV
• North
• West
• South
KY
• N-Central
• East
• West
TN
• West
• East

1980 Characteristics of the Regional Coal-Fired Power Plants

State	No. of Units[a]	SO_2 Emissions[a] (ktpy)	Coal Capacity[a] (GW)	Avg SO_2 Rate[a] (lbs/MBtu)
OH	99	2221	22.31	4.06
IN	66	1588	14.58	4.35
PA	70	1427	17.93	2.76
MO	41	1214	9.97	4.82
IL	59	1136	15.15	2.98
WV	33	966	14.46	2.79
TN	37	950	9.41	3.77
KY	54	947	11.82	3.56
Total	449	10,449	116.23	3.57

[a] Includes scrubbed as well as unscrubbed plants. Total 1980 FGD capacity in the region was 9.72 GW.

least cost strategy for each state.[8] A third option allowed the combined emission reduction for the eight states to be achieved from sources anywhere within the region. A marginal cost of control curve for the region as a whole was developed in precisely the same way as for an individual state to arrive at this solution. This simulates scenarios in which efficient interstate trading is assumed to be feasible.

For all of the above cases three scenarios regarding available SO_2 control technology were modeled. First, it was assumed that only conventional wet FGD systems would be available as an alternative to coal switching or blending. Next, we allowed dry FGD systems to compete with wet FGD for retrofit applications. Finally, we assumed that LIMB technology also becomes a commercial option for wall-fired and tangentially-fired boilers by 1992.[9] For each of these cases the effect of several performance and economic variables on the costs of control and the degree of technology implementation were examined.

The plant operating factors varied in the analysis included the capacity factor and unit lifetime. Nominally, a 45-year lifetime was assumed for coal-fired plants except where an earlier retirement year had been reported. We also considered a life extension scenario which added 20 years to the useful life of all units larger than 100 MW. The levelized capacity factor over each unit's remaining life was assumed to lie between 35% and 65%, depending on unit age.[10] In analyzing plants with multiple units we further assumed that FGD systems would be retrofitted on individual units greater than 400 MW, but that smaller units would be grouped into larger systems wherever possible to take advantage of economies of scale.[11] Limited comparisons with results of a unit-by-unit analysis also were undertaken.

Finally, several scenarios regarding the future price trends for coals of different sulfur contents also were incorporated in the analysis. These are discussed later in the context of model sensitivity analyses. Nominal assumptions (which reflect real increases in low sulfur coal prices) are included in Table 1.

Results for Wet FGD vs. Coal Switching

Figure 2 summarizes the results of 99 cases reflecting different assumptions regarding emission reduction requirements, method of implementation, and coal use constraints. Figure 2(a) indicates the percent of total eligible capacity in the eight state region (101 GW) choosing FGD with only wet limestone systems assumed available. FGD capacity increases significantly as the emission reduction requirement becomes more stringent, though the absolute values depend upon the coal choice constraint and the method of allocation to sources. The ranges in Figure 2(a) correspond to FGD capacities of 16-26 GW for a 50% reduction, 35-58 GW for a 65% reduction and 61-72 GW for an 80% reduction with an unconstrained choice of coals. In general, FGD retrofits are accompanied by a preference for less expense higher sulfur coals to minimize overall

---

[8] This is typically assumed to involve intra-state trading. However, a simple multi-tiered system of emission caps based on the cost-effectiveness of control also may closely approximate a least cost solution [12].

[9] Inputs to the model include the construction time for each SO_2 control device considered. The longest lead time determines the year in which control strategy decisions are made. In these cases, a three year construction time is assumed for FGD, so that decisions for 1995 are actually made in 1992.

[10] A capacity factor of 35% was assigned to units with only one year of remaining life (in the compliance year), increasing linearly to 50% for a 10-year life and to 65% for a life of 20 years or more.

[11] For the eight states in this study, 43% of the coal-fired capacity in 1980 was in unit sizes less than 400 MW.

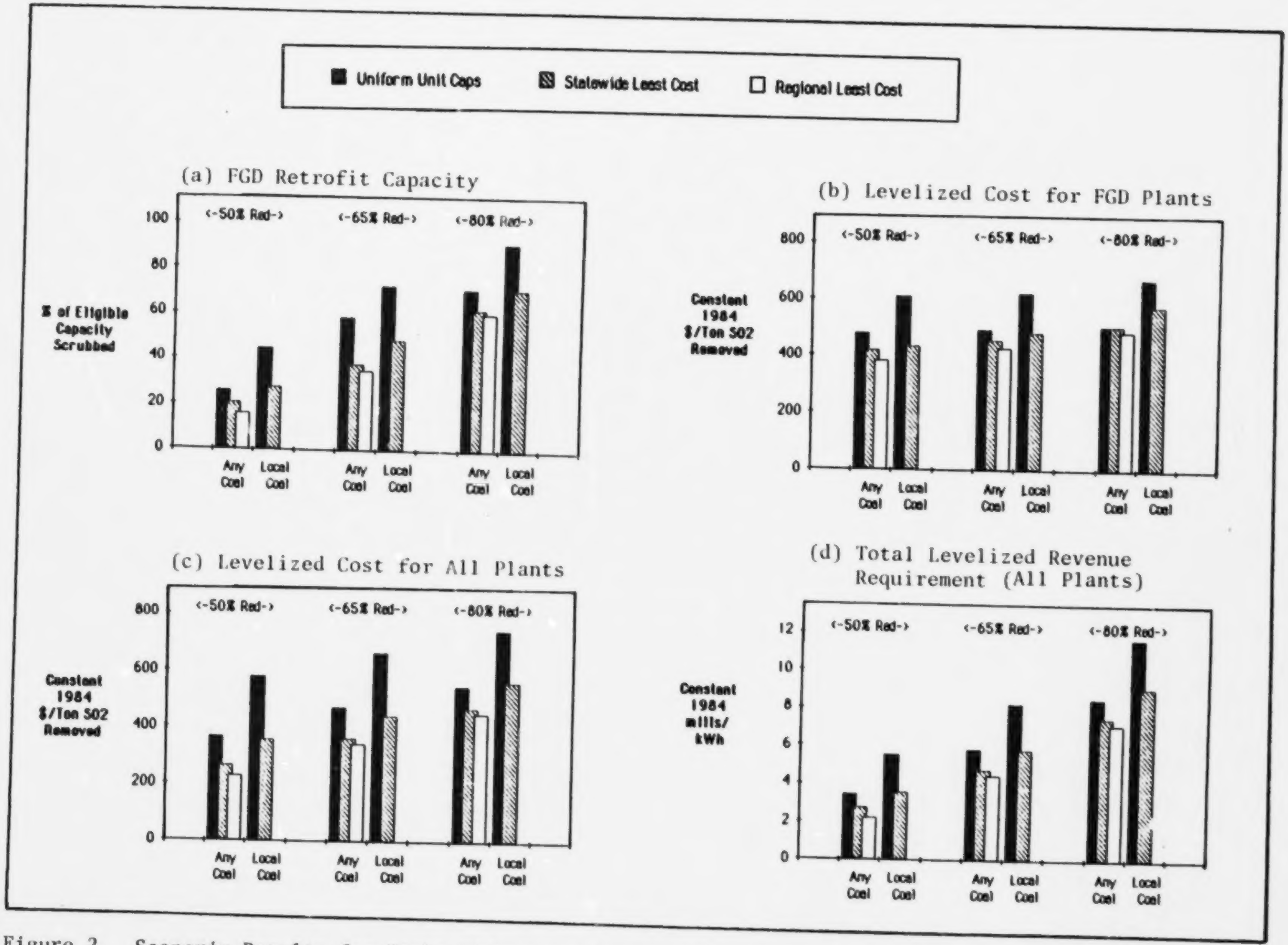


Figure 2. Scenario Results for Eight Midwestern States With One FGD Option (Wet Limestone Scrubbing)

costs. Across all scenarios, FGD capacity increases by 7 to 20 GW when only local coals are used, reflecting higher average sulfur contents.

Among the three implementation schemes (uniform unit caps, state least cost, and regional least cost) the uniform cap strategy yielded the largest amounts of FGD capacity for a given level of emissions reduction. However, much of this reflects a relatively low overall SO_2 removal efficiency (often only 50%) which is achieved by scrubbing only part of the gas stream and bypassing the rest. In contrast to this, the least cost solutions employ full scrubbing of less capacity. The economic benefit of this approach is seen in Figures 2(b), which shows the average levelized cost per ton of SO_2 removed for plants retrofitting FGD. These range from $420 to $675/ton of SO_2 (constant 1984 dollars) across the set of cases shown.[12] Average costs using local coals are 9-24% higher than with an unconstrained coal choice, depending on the implementation plan. The regional and state least cost strategies produce levelized FGD costs that averaged 20% lower than corresponding cases with uniform caps for regional reductions of up to 65%. For an 80% reduction results were similar to uniform caps.[13]

Table 6 shows the sensitivity of predicted FGD use to changes in several technical and economic assumptions for the statewide least cost strategies with a 65% overall SO_2 reduction requirement. Varying the nominal retrofit cost premium between 5% and 55% changed the total FGD capacity by approximately ± 2500 MW from the baseline scenario. Similar effects were found from varying the real cost of capital, the real escalation of control system O&M costs, the in-plant cost of electricity, and the cost of ESP upgrades for coal switching. Varying the assumed unit capacity factors also produced only relatively modest changes in total FGD capacity.

A much more significant effect is seen for the 20-year plant life extension scenario. The combination of higher expected plant utilization and longer amortization periods for capital equipment causes an additional 9.8 GW of eligible capacity to choose FGD. The effect is even more pronounced when the life extension program is combined with a lower real interest rate. Here, the FGD retrofit capacity climbs by an additional 6.8 GW to a total of 54 GW.

The particular coal price and availability assumptions against which future FGD capacity and costs are evaluated is clearly a critical factor in analyzing scrub-or-switch decisions [13]. This is especially true for low to moderate emission reduction requirements, and for plants using high sulfur coals. In Table 6 we show the results of several scenarios involving different coal supply and price assumptions. The first is the "local coal" case shown earlier, whose objective primarily is to avoid disruptions of the high sulfur coal industry. FGD capacity increased by 11.3 GW in this scenario, in which coal washing also is used more extensively for sulfur removal. The next case assumes that only current (1980) coals are used at each facility (with no additional coal cleaning). Thus, to achieve the overall statewide reduction at lowest cost, some plants are selected for FGD retrofits while others employ no new SO_2 controls. Results for this case show an additional 7.7 GW of FGD capacity in the region, with a 22% increase in the average cost per ton of SO_2 removed by FGD relative to the base case. The remaining scenarios show

---

[12] Note that these figures also reflect savings in fuel cost by plants switching to less expensive coals in conjunction with FGD; hence, they are generally lower than costs where no coal switching is considered.

[13] The full effect of different implementation methods and coal constraints is seen in Figures 2 (c) and (d), which show the levelized SO_2 removal cost and revenue requirement for the total scenario, including plants that do not use FGD. Statewide least cost strategies yield costs that are 15-40% lower than corresponding unit cap cases, while regional strategies reduce average costs by an additional 3-10%. The feasibility of implementing the regional approach, however, appears much more limited than the statewide least cost method [12].

Table 6

Sensitivity Analysis for a 65% Statewide Least Cost Reduction With a Conventional (Wet Scrubbing) FGD Option (Results for Scrubbed Plants Only)

Case No.	Description	Value	FGD Cpcty [%]	TotCap Cost [$/kW]	Revenue Reqmt [m/kWh]	Abtmnt Cost [$/Tn]
1	Base Case	Table 1	37.4	246.	9.38	457.
2	Higher Retrofit Factors[a]	1.55	35.2	293.	10.63	496.
3	Lower Retrofit Factors[a]	1.05	40.2	200.	7.70	405.
4	Higher ESP Upgrade Costs[b]	(Variable)	39.2	247.	9.31	459.
5	Lower Real Interest Rate[c]	4.10%	40.4	241.	7.51	393.
6	Real O&M Cost Escalation[d]	0.5%/yr	37.3	245.	9.88	479.
7	Lower In-Plant Power Cost	50 mills/kWh	40.1	247.	8.27	431.
8	1980 Capacity Factors		35.1	245.	9.88	485.
9	Uniform Capacity Factors	65%	38.0	247.	9.34	451.
10*	Unit Life Extension	20 yr (>100 MW)	45.7	251.	7.48	397.
11*	Cases 10 + 5		52.3	245.	5.93	333.
12	Local Coals Only		48.6	251.	9.48	483.
13	Current Coals Only		56.2	261.	12.20	557.
14	Higher Real Coal Escal[e]	1.5/1.5/0.5/0.25	40.2	248.	8.82	453.
15	Lower Real Coal Escal[e]	1.0/0.5/0.0/0.0	35.5	248.	9.73	455.
16	Case 15 + Lower Trans Escal[f]	0.5%/yr	30.0	243.	10.31	459.
17	Case 15 + No Trans Escal[f]	0.0%/yr	28.4	243.	10.35	465.
18	Local Coals + Case 2		45.5	302.	10.76	524.
19	+ Case 3		50.0	205.	8.46	435.
20	+ Case 5		49.9	246.	8.24	423.
21	+ Case 6		46.7	253.	10.18	503.
22	+ Case 8		46.0	251.	10.45	515.
23*	+ Case 10		53.7	257.	8.55	410.
24*	+ Case 11		59.4	251.	6.89	349.

Footnotes:

[a] Applied to all SO2, TSP, and solid waste capital costs
[b] Based on calculated increase in required plate collector area
[c] Corresponds to an 8.5% inflation rate or a 10.3% weighted cost of capital
[d] Applied to all plant O & M costs except utilities
[e] Applied to coal sulfur categories defined in Table 1
[f] Applied to all coals and transport modes

* Note that these cases involve an additional 3 GW of eligible capacity and longer cost amortization periods which affect direct comparisons with results of other scenarios

the effect of simple price escalation rates for coals of different sulfur content. Our nominal assumption reflected estimated premiums for lower sulfur eastern coals based on a recent study for EPRI [14]. In the base case, coal transportation costs for rail, barge, truck and lake vessel also were assumed to escalate in real terms as a result of recent deregulation. Escalation rates were applied to 1980 minemouth coal and transportation price estimates developed by Morrison [15]. Alternative assumptions are shown in Table 6. Overall, the variations considered here produced moderate to significant changes in total FGD capacity. For the 65% reduction level, total capacity fell by about 9,000 MW with lower coal and transportation prices and rose by 3000 MW with higher prices. A wider range of coal and transportation price scenarios (including differential rates by region and by transport mode) could be expected to produce a still broader range of FGD capacity estimates, particularly for low to moderate SO_2 reduction requirements. For higher abatement levels, FGD capacity is less sensitive to coal price assumptions [15].

Impact of Dry FGD Retrofits

In a second series of model runs, lime spray dryer FGD systems were assumed to be a technically viable retrofit option for high sulfur coal, in addition to wet FGD. However, for the nominal assumptions indicated earlier, dry FGD was selected by no more than 3% of the eligible capacity at all three SO_2 reduction levels. The major factor affecting this was the cost of particulate control. With a $19/kW upgrade cost for existing ESP in lieu of a new baghouse collector, dry systems accounted for more than half the total FGD capacity for the 50% and 65% SO_2 reduction requirements, falling to 20% of the market for an 80% reduction. Those cases assumed that overall SO_2 removal performance was not significantly altered by replacing a baghouse with an ESP.[14] Scenarios combining lower particulate costs with an improvement in reagent stoichiometry gave dry FGD a further advantage over wet systems, though it remains to be seen whether this can actually be achieved with higher sulfur coals. Nonetheless, these scenarios suggest that technical advances in ESP upgrades and dry scrubber performance could make this technology competitive for retrofit applications should future SO_2 controls be required.

Impact of LIMB Commercialization

A final set of cases assumed that LIMB also becomes a commercially available retrofit option in the next decade. Figures 3(a) and (b) show the effect this has on control technology selection under two implementation schemes.

With uniform emission caps (Figure 3a), LIMB and wet FGD are the preferred retrofit technologies for the low (50%) and intermediate (65%) statewide sulfur reduction levels. Though the total wet FGD capacity for these cases equals or exceeds that of LIMB, much of this again reflects situations where partial scrubbing is used to obtain relatively low overall SO_2 emissions reductions. Thus, the "equivalent fully scrubbed capacity" for wet FGD is substantially lower than the values shown. As the SO_2 reduction requirement increases to 80%, LIMB capacity falls to less than 10 GW (from an earlier high of 33 GW), with the more efficient dry FGD systems coming into wider use. In all cases, more SO_2 removal technology is employed when only local coals are used in each state.

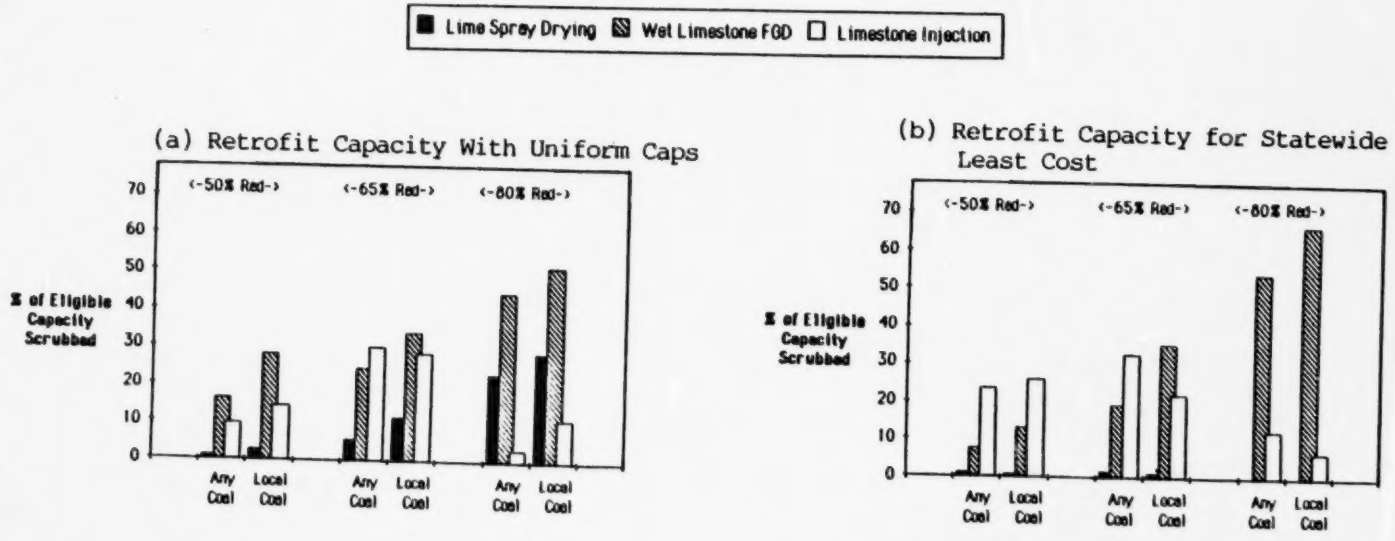
Figure 3(b) presents a somewhat different picture of how these technologies would compete under a statewide least cost strategy. The major difference is that dry FGD

---

[14] Preliminary data suggest that this may be achieved provided the approach to saturation temperature is adequately controlled [16].

(a) Retrofit Capacity With Uniform Caps

(b) Retrofit Capacity for Statewide Least Cost



(c) Retrofit Cost With Uniform Caps

(d) Retrofit Cost for Statewide Least Cost

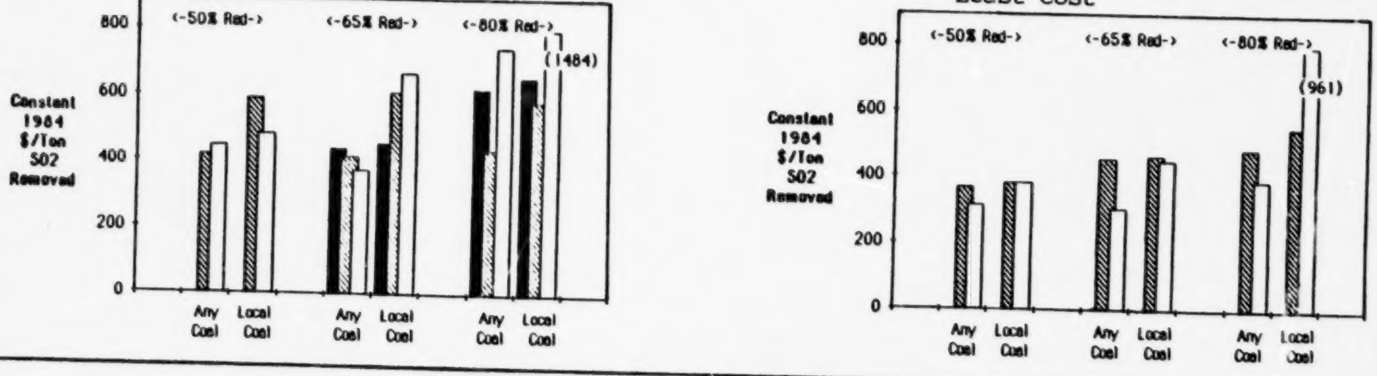


Figure 3

Control Technology Selection With Multiple FGD Options systems no longer emerge as a strongly preferred option in any of the scenarios. On the other hand, LIMB is utilized more widely for the lower reduction requirements, while wet FGD use increases for the higher reduction cases. The reasons for this are related to the marginal costs of SO_2 removal at each facility, and for each state as a whole. Dry FGD systems are not widely selected because the marginal costs of SO_2 removal typically exceeds that of LIMB at low total abatement levels, and that of wet FGD at high abatement levels. Thus, its use is limited to less than 2% of the eligible capacity under the nominal assumption requiring a new baghouse collector.

The corresponding averaga costs of SO_2 removal are shown in Figures 3(c) and (d) for the uniform cap and statewide least cost solutions, respectively. The relative cost of each option depends upon the particular scenario one looks at, but in general, average costs again are seen to rise with increasing abatement level, and are higher when only local coals are used.

Figure 4 shows the overall capacity and average costs for plants retrofitting wet and dry SO_2 removal systems. To put this in perspective, we also show the levelized costs for all plants, including those which blend, switch coals, take no action, or retire prematurely as part of an emission reduction strategy. Figure 4(a) shows that across the five implementation and coal choice scenarios shown for each reduction level, total FGD capacity ranges from 25 to 46 GW for a 50% reduction, 54 to 74 GW for a 65% reduction, and 66 to 92 GW for an 80% reduction. These ranges reflect 5 to 20 GW more scrubbed capacity than the corresponding ranges with wet removal systems only (Figure 2a), primarily because of the availability of LIMB. The lowest FGD capacity requirements are again found for the least cost state or regional strategies, both of which produce similar results for a given emission reduction level.

Figure 4(b) shows the average levelized costs for plants retrofitting scrubbers. These are approximately 20% lower than when only wet FGD systems are available for overall SO_2 reductions of up to 65%. This cost savings falls to 10% when only local coals are used, and diminishes still further at higher reduction levels. Again, FGD costs are highest when the coal choice and implementation method are most constrained.[15]

Table 7 shows results of a sensitivity analysis for the 65% statewide reduction level with multiple SO_2 removal options. Within the limitations of this study the most important technical factor influencing the choice among SO_2 control devices was the method and cost of particulate removal for LIMB and spray dryer systems.[16] When the nominal assumption of a baghouse retrofit was relaxed to allow existing ESPs to be upgraded at lower cost, the use of dry systems (particularly LIMB) increased significantly. Overall, two-thirds of the regional capacity now employed some form of SO_2 removal system, compared to a little more than one-third with only wet FGD systems available. Even for an 80% overall abatement level (not shown in Table 7), LIMB capacity remained relatively high (26 GW) with lower TSP control costs. The incremental effects of lower reagent requirements (Case 7) or higher boiler modification costs (Case 6) were comparatively small. The most dramatic

---

[15] For the scenario as a whole, the potential economic benefits of a flexible implementation plan again are seen in Figures 4(c) and (d) which show the overall SO_2 removal cost and annual revenue requirement for each scenario in constant 1984 dollars. As in Figure 2(d), savings of 15-40% are found for the statewide least cost solutions. In the most restrictive scenarios (uniform emission caps, high SO_2 reduction requirements, and only local coals), the average SO_2 removal cost for the region as a whole is actually higher than for plants retrofitting FGD. This is because of plants where it is more economical to retire prematurely, with the cost of foregone power production charged to the scenario.

[16] We have not analyzed the effects of higher removal efficiencies, other sorbent types, or other system designs which could influence this conclusion.

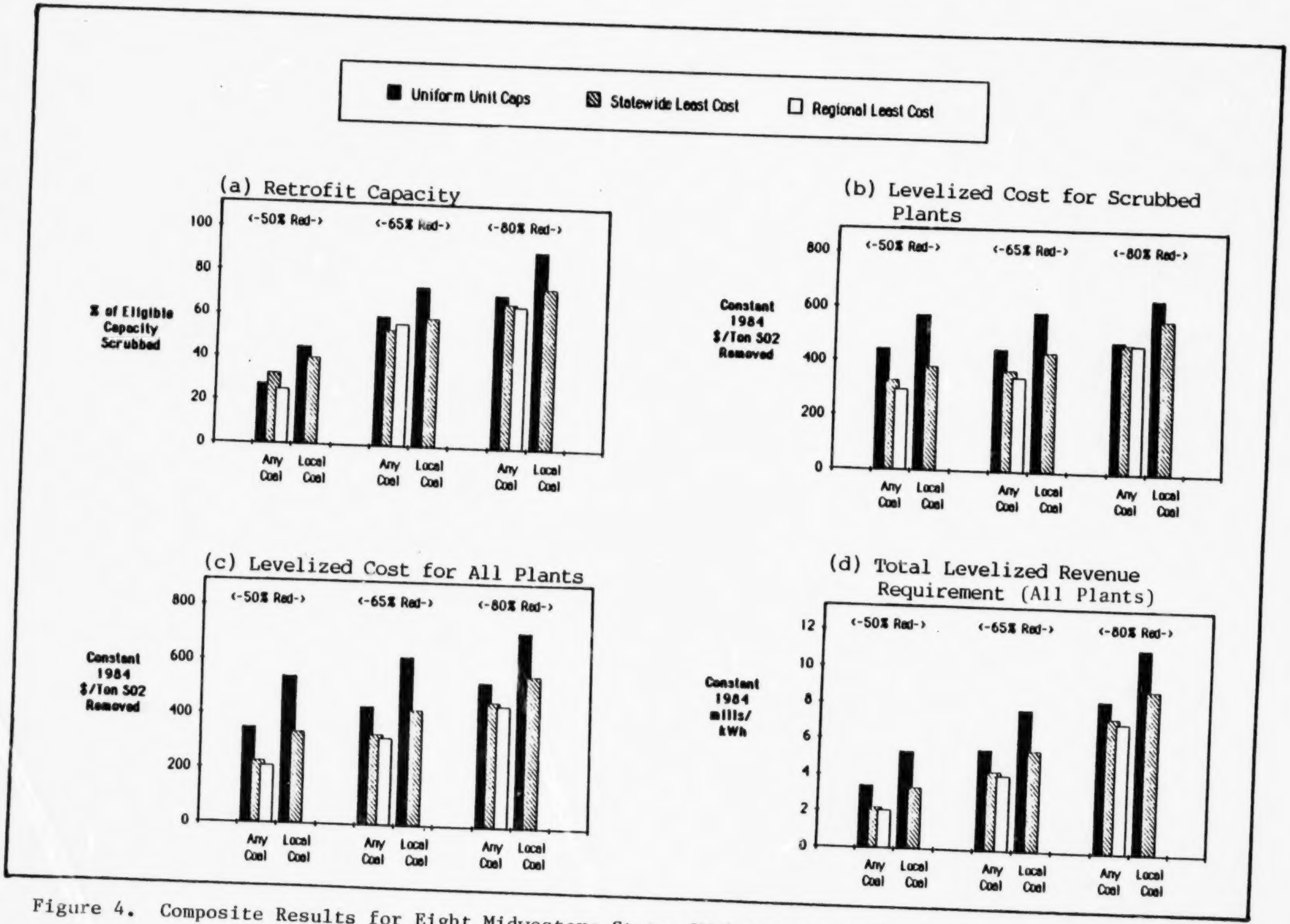


Figure 4. Composite Results for Eight Midwestern States With Multiple FGD Options

Table 7

Sensitivity Analysis for a 65% Statewide Least Cost Reduction With Multiple SO_2 Removal Options (Results for Scrubbed Plants Only)

Case No.	Description	Value	Wet Limestone Capacity [%]	Spray Drying Capacity [%]	Limestone Injection Capacity [%]	Total Abtmnt Cost [$/Tn]
1	Base Case	Table 1	19.2	1.9	32.6	373.
2	1980 Capacity Factors		22.8	0.8	24.6	426.
3	Higher Retrofit Factors[a]	1.55	19.2	1.9	32.4	419
4	Real O&M Cost Escalation[b]	0.5%/yr	19.2	1.9	32.6	390.
5	Lower TSP Control Costs[c]	$18.56/kW	11.3	8.0	47.9	310.
6	Case 5 + Higher LMB Modif Cost[d]	$24.60/kW	13.3	7.6	43.6	320.
7	Case 5 + Lower Reagent Use[e]	2.5/0.95	9.8	8.7	49.5	297.
8*	Unit Life Extension	20 yr (>100 MW)	18.0	2.8	52.0	301.
9*	Cases 7 + 8 + Lower Intrst[f]	4.10%	7.7	12.3	65.7	178.
10	Local Coals Only		35.6	1.3	22.1	443.
11	Current Coals Only		46.6	0.6	16.5	546.
12	Higher Real Coal Prices[g]	1.5/1.5/0.5/0.25	22.5	1.5	31.0	387.
13	Lower Real Coal Prices[g]	1.0/0.5/0.0/0.0	18.6	1.5	31.6	381.
14	Case 13 + Lower Trans Escal[h]	0.5%/yr	16.0	1.0	30.1	381.
15	Cases 14 + 5		4.7	7.5	50.8	309.
16	Local Coals + Case 5		19.0	6.6	43.1	388.
17	+ Case 7		18.5	7.1	43.5	377.
18*	+ Case 8		28.5	2.0	46.9	362.
19*	+ Case 9		17.9	11.5	59.1	249.
20	Current Coals + Case 5		36.7	3.5	34.5	515.

Footnotes:

[a] Applied to all SO2, TSP, and solid waste capital costs
[b] Applied to all plant O & M costs except utilities
[c] Assumes ESP upgrade available for dry SO2 removal systems
[d] Boiler modification costs for LIMB assumed to be twice the nominal value
[e] Assumes stoichiometries of 2.5 for LIMB and 0.95 for spray dryers to achieve 50% and 70% SO2 removal, respectively
[f] Corresponds to an 8.5% inflation rate or a 10.3% weighted cost of capital
[g] Applied to coal sulfur categories defined in Table 1
[h] Applied to all coals and transport modes

*Note that these cases involve an additional 3 GW of eligible capacity and longer cost amortization periods which affect direct comparisons with results of other scenarios changes were found for a scenario in which R&D improvements were combined with a major program of plant life extension plus a more favorable long-term outlook for real interest rates (Case 9). Here, fully 84% of the total eligible capacity in the region chose some form of SO_2 removal device (mostly LIMB).[17] While this is clearly an extreme scenario, it does suggest that technical advances in combination with other factors can have a significant effect on least cost SO_2 removal strategies.

Table 7 also shows the different quantitative results that emerged for several alternative coal price and choice constraints. For the local coal scenarios where only washed and unwashed coals produced within each state are available for switching, more wet FGD and less dry system capacity was found. The use of dry systems decreases further for the most restrictive case where only current coals are used at each plant. These scenarios again produced the highest control costs of any cases considered in this analysis. On the other hand, greater use of dry removal technology is seen with lower coal and transportation prices, which allows more washed and medium sulfur coals to be used. A more comprehensive analysis of alternative assumptions remains for further study.

CONCLUSIONS AND CAVEATS

Our principal objective in this paper has been to describe and illustrate some of the analytical capabilities of a newly developed computer model of the U.S. electric utility sector, with emphasis on technical factors affecting control strategy selection and the role of FGD. Illustrative results for an eight-state region of the midwest showed how future FGD retrofit capacity and costs vary with emission reduction requirements, SO_2 removal options, control technology performance variables, power plant operating characteristics, coal use constraints, reduction implementation schemes, and general economic factors. This is a much broader range of parameters than has been considered prior to now using other available modeling tools. Some of the results suggested by this analysis are that:

- The use of coal cleaning in conjunction with wet and dry SO_2 removal systems often yielded the most economical approach to sulfur emissions reductions in the midwest, particularly if only local coals are employed.

- The availability of dry SO_2 removal options for plants using medium and high sulfur coals can have a marked influence on future FGD retrofit capacity and cost, particularly for overall SO_2 reductions in the range of 50-65%.

- If SO_2 removal performance for LIMB and spray dryer systems is able to meet current expectations, the most critical factor affecting their adoption will be the requirements and cost of particulate control equipment. For the cases analyzed here, the ability to upgrade and utilize an existing ESP rather than retrofit a new baghouse collector produced significant increases in the selection of dry SO_2 removal systems in competition with conventional wet limestone FGD.

- The future availability of LIMB technology achieving 50% sulfur removal had the largest impact on the choice of SO_2 control systems for the three options examined, particularly for the intermediate (65% overall) SO_2 reduction requirement. This was predicated on the ability to widely retrofit direct injection systems on existing wall-fired and tangentially-fired units, which still remains to be demonstrated.

---

[17] A maximum unit life of 30 years (equivalent to new plants) was assumed for these cases, though many plants were still below this.

- The potential effect of plant life extension programs on the attractiveness of FGD is significant. Scenarios with 20-year life extensions yielded significant increases in total FGD capacity together with decreases in the levelized cost of sulfur removal.

- The way in which SO_2 emission reductions are allocated to individual sources can have a significant effect on control technology selection, the cost of FGD, and the total FGD capacity required to meet a particular emission reduction level. Of the three schemes analyzed in this study, (uniform caps, statewide least cost and regional least cost) the "statewide least cost" approach is suggested as the most promising option for further consideration.

The results of sensitivity analyses presented in this paper also affirmed the findings of many previous studies regarding the importance of such factors as coal prices and overall SO_2 abatement requirements on the level and cost of FGD retrofits. Results for other regions would be expected to show similar sensitivities.

Obviously, a number of important caveats must accompany this analysis. Certainly, additional site-specific factors not currently reflected in the model or its associated data bases will affect FGD retrofit decisions and costs for particular plants or units. As new information of this type becomes more readily available its incorporation into the simulation framework will provide an important refinement. The same is true for improved information on coal characteristics and transportation constraints, which also may affect the feasibility of coal switching at individual facilities.

Much more also can be done analytically using additional model components not utilized in this study. This would include the simulation of power plant dispatching to evaluate the annual costs of FGD and optimal selection of SO_2 control options in response to more detailed projections of future electricity demand (including price elasticity effects), relative power generation costs, financial and tax treatment of utilities, coal price and availability assumptions, and other factors of interest in addition to control technology design. Thus, the analysis presented here is only indicative of potential model applications for utility planning, policy analysis, market analysis and research management.

ACKNOWLEDGEMENTS

The work described in this paper was supported under a grant from the Claude Worthington Benedum Foundation. The authors acknowledge the valuable assistance of Mr. W. Gooding, J. Salmento and Dr. H. Dowlatabadi in preparing the software and data bases used in this paper. We are also grateful to the many individuals whose advice, comments and insights have contributed to the development of this model over the past several years.

REFERENCES

1. Acid Rain and Transported Air Pollutants: Implications for Public Policy, U.S. Congress, Office of Technology Assessment, OTA-0-204, Washington, D.C., June 1984.

2. Stukel, J.J., et al., The State Level Advanced Utility Simulation Model: Analytical and Program Documentation, 6 volumes, Universities Research Group on Energy, University of Illinois at Urbana-Champaign, Urbana, Illinois, November 1984.

3. Skea, J.F., Utility Control Strategy Model User's Manual (Draft), Center for Energy and Environmental Studies, Carnegie-Mellon University, Pittsburgh, Pennsylvania, January 1984.

4. Bloyd, C.N., et al., The State Level Advanced Utility Simulation Model Analytical Documentation, Chapter 5: The Pollution Control Module, Universities Research Group on Energy, University of Illinois at Urbana-Champaign, Urbana, Illinois, November 1984.

5. Skea, J.F. and E.S. Rubin, The State Level Advanced Utility Simulation Model Analytical Documentation, Appendix C: Coal Cleaning Methodology, Universities Research Group on Energy, University of Illinois at Urbana-Champaign, Urbana, Illinois, November 1984.

6. Anders, W.L. and R.L. Torstrick, Computerized Shawnee Lime/Limestone Scrubbing Model Users Manual TVA/OP/EDT-81/15, Tennessee Valley Authority, Muscle Shoals, Alabama, March 1981. (Also, private communications, 1982-85.)

7. Molburg, J.C. and E.S. Rubin, "Air Pollution Control Costs for Coal-to-Electricity Systems," *Journal of the Air Pollution Control Association*, Vol. 33, No. 5, May 1983.

8. Skea, J.F. and E.S. Rubin, "An Assessment of Coal Washing as a Strategy for Mitigating Acid Deposition," Paper No. 84-27.3, *Proc. of 1984 Annual Meeting*, Air Pollution Control Association, Pittsburgh, Pennsylvania, June 1984.

9. Lachapelle, D.G., N. Kaplan and J. Chappell, "EPA's LIMB Cost Model: Development and Comparative Case Studies," Paper 6H, *Proc. of First Joint Symposium on Dry* SO_2 *and Simultaneous* SO_2/NO_x *Control Technologies*, Electric Power Research Institute/U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, November 1984.

10. Yaeger, K.E., "An Assessment of Control Technology Options," *Proc. of 1985 American Power Conference*, April 1985.

11. Technical Assessment Guide EPRI P-2410-SR, Electric Power Research Institute, Palo Alto, California, May 1982.

12. Skea, J.F. and E.S. Rubin, "Least Cost Strategies for Regional SO_2 Emission Reductions," Paper No. 85-1B.6, *Proc. of 1985 Annual Meeting*, Air Pollution Control Association, Pittsburgh, Pennsylvania, June 1985.

13. Agenda of Critical Issues: Coal Price and Availability, EPRI EA-3750, Prepared by. Temple, Barker and Sloane, Inc., for the Electric Power Research Institute, Palo Alto, California, October 1984.

14. Effects of Resource Depletion on Future Coal Prices, EPRI EA-3733, Prepared by ICF, Inc., for the Electric Power Research Institute, Palo Alto, California, October 1984.

15. Morrison, M.J., A Linear Programming Model to Examine Sulfur Dioxide Control Strategies for Coal-Fired Utility Plants, Center for Energy and Environmental Studies, Carnegie-Mellon University, Pittsburgh, Pennsylvania, August 1983.

16. Private Communication with Tennessee Valley Authority, Chattanooga, Tennessee, 1985.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

Session 2: COMMERCIAL STATUS OF FGD

Stuart M. Dalton, Chairman
Electric Power Research Institute
Palo Alto, CA

THE PRESENT AND FUTURE STATUS OF FGD IN THE UNITED STATES

Robert W. McIlvaine

The McIlvaine Company
2970 Maria Avenue
Northbrook, IL 60062

ABSTRACT

More than 50,000 megawatts of FGD systems are in operation in the United States. More than 100,000 megawatts will be in operation by 1991. An upsurge in new boiler orders beginning in the next few years will raise the FGD total to close to 175,000 megawatts in the U.S. by the late 1990's. Acid rain control could be an important factor in determining this total but variations in peak load demand and boiler replacement rates will be more significant long term. The commercial situation is constantly changing. Architect engineers, boiler companies, scrubber system designers and component suppliers are attempting to take more responsibility. This is spurring competition among these groups as well as among individual suppliers. Integration, new technology and internationalization are also shaping the competitive environment.

The title of this session is the "Commercial Status of FGD". Webster lists a variety of definitions for the word commercial. One of definitions is "being of an average or inferior quality." I am sure the organizers of this conference did not have this definition in mind when they labeled the sessions. Another definition of commercial is "designed for a large market". Some of the scrubber system suppliers might argue that the industry does not qualify under this definition either. On the other hand the flue gas desulfurization industry has grown from zero to the largest single air pollution control market in a period of less than 20 years. How big is this market presently? How big will it be? These are some of the questions which this speech will address.

Another definition of commercial is "relating to the buying and selling of commodities." The industry is being put to the test under this definition with the present variety of methods for designing a system. Is there a buyer and a seller when a major utility assumes the system responsibility? Where does the traditional supplier (the scrubber system designer) fit into an industry when architect engineers want to purchase components, when utilities design their own systems and when component suppliers are stepping up their selling efforts to sell directly to the end user.

Commercial is also defined as "with regard for profit". Is there adequate profit potential in the industry and for whom? Take nozzles as an example. How much of the profit and the responsibility should go to the manufacturer of the ceramic material, to the nozzle supplier, to the scrubber supplier or to the constructor who may furnish the nozzle as part of a boiler-scrubber system package.

HISTORY

To answer some of the questions we have posed, let's take a quick overview of FGD history in the United States. The first installation could hardly be called commercial by any of the above definitions but it was a beginning. A mobile bed scrubbing system was installed at Union Electric Company in 1968. Limestone was injected along with coal in the boiler. The scrubber and much of the system was constructed of carbon steel and a so-called corrosion resistant coating applied. This descriptive adjective proved only accurate for a few hours and subsequent corrosion and process problems resulted in the ultimate demise of this system. On the other hand, a tremendous amount of information was learned that had not been apparent in earlier small scale tests at Detroit Edison or previously in the laboratory. Designers quickly learned the disadvantages of injecting the limestone with the coal and learned the importance of process chemistry.

Many of the early systems employed mobile bed scrubbers or even venturis which remove both flyash and SO_2. The demand for higher reliability and the necessity for greater flyash collection efficiency soon dictated the use of a precipitator for flyash removal followed by the scrubber for SO_2 removal. Some of the early systems were designed to produce a useable product. Catalytic oxidation was an early casualty, but the magnesium oxide and sodium systems proved to be a viable means to obtain a saleable sulfur or sulfuric acid end product.

At first the effort in the industry was primarily a combination of boiler and scrubber company talents. Boiler companies rapidly learned from the scrubber companies and in combination or competition offered complete turnkey systems. Architect engineers were generally unfamilar with the technology and were more than willing to play a minimal role. The components suppliers by and large were also completely unfamiliar with the problem and there were no suitable nozzles, mist eliminators, or for that matter dampers and pumps. For this reason the scrubber system designers were heavily involved in component research and development as well as process design.

Today, seventeen years later, the situation is much more complex. A great deal of research is being done by the utilities themselves through the Electric Power Research Institute as well as individually. Architect engineers in their engineering or construction role are also active in research and development and in some cases are offering a proprietary process to utilities. Component manufacturers have realized a sizeable potential in the FGD market place and have designed nozzles, valves and dampers specifically for FGD service. It is not unusal for component sales to be directly to the end user or to the AE as opposed to the scrubber process supplier. This is particularly true in the case of older FGD systems which are being substantially revised and modernized.

The situation is even more complex in the case of spray dryer systems. The utilities had a major role in the early development of the spray dryer systems. Secondly, there are several players in the spray dryer game other than traditional suppliers. They include the manufacturer of the spray dryer and the manufacturer of the fabric filter. These are the two largest and most important components in the spray dryer system and are not necessarily manufactured by the process designer. The result is that the knowledge and responsibility for the design and purchase of a modern spray dryer system is much more diffused than the design and responsibility for the early wet systems. The question is whether this trend will continue, stabilize or reverse itself. Let's examine some of the present industry statistics before making any predictions.

PRESENT STATUS OF FLUE GAS DESULFURIZATION IN THE UNITED STATES

There are presently 124 FGD systems operating in the United States. They purify gases from 50,000 MW of electrical generating capacity. This means that the average size of an individual system is over 400 MW. In most cases the components are some multiple number of the system. The utility FGD survey as of September 1984 shows an additional nearly 15,000 MW of systems under construction, 9,000 MW in the contract awarded category, 2500 MW in the letter of intent category, just under 2,000 MW in the bid evaluation stage and another 27,500 MW in the process of considering FGD systems. Figure 1 shows the capacity controlled with FGD systems from 1975-1992. Only 17% of coal-fired capacity is presently controlled by FGD systems. By 1992 nearly a 1/3 of the boilers will be controlled by FGD systems given the present utility plans.

Figure 2 is a graph prepared by The McIlvaine Company from data appearing in the September 1984 EPRI project summary and shows the predominance of wet limestone systems for SO_2 removal. Over 50% of the systems use limestone alone or with alkaline flyash. Some 6% of the systems use sodium carbonate either as part of a double alkali system or as the single alkali. Whereas in other countries gypsum is the primary byproduct of FGD systems, in the United States only 0.4% of all the systems end up with gypsum as a byproduct. The magnesium oxide and Wellman-Lord processes with sulfuric acid as an end product account for 5.7% of the total. Dry systems account for only 5.7% of the total as of September 1984.

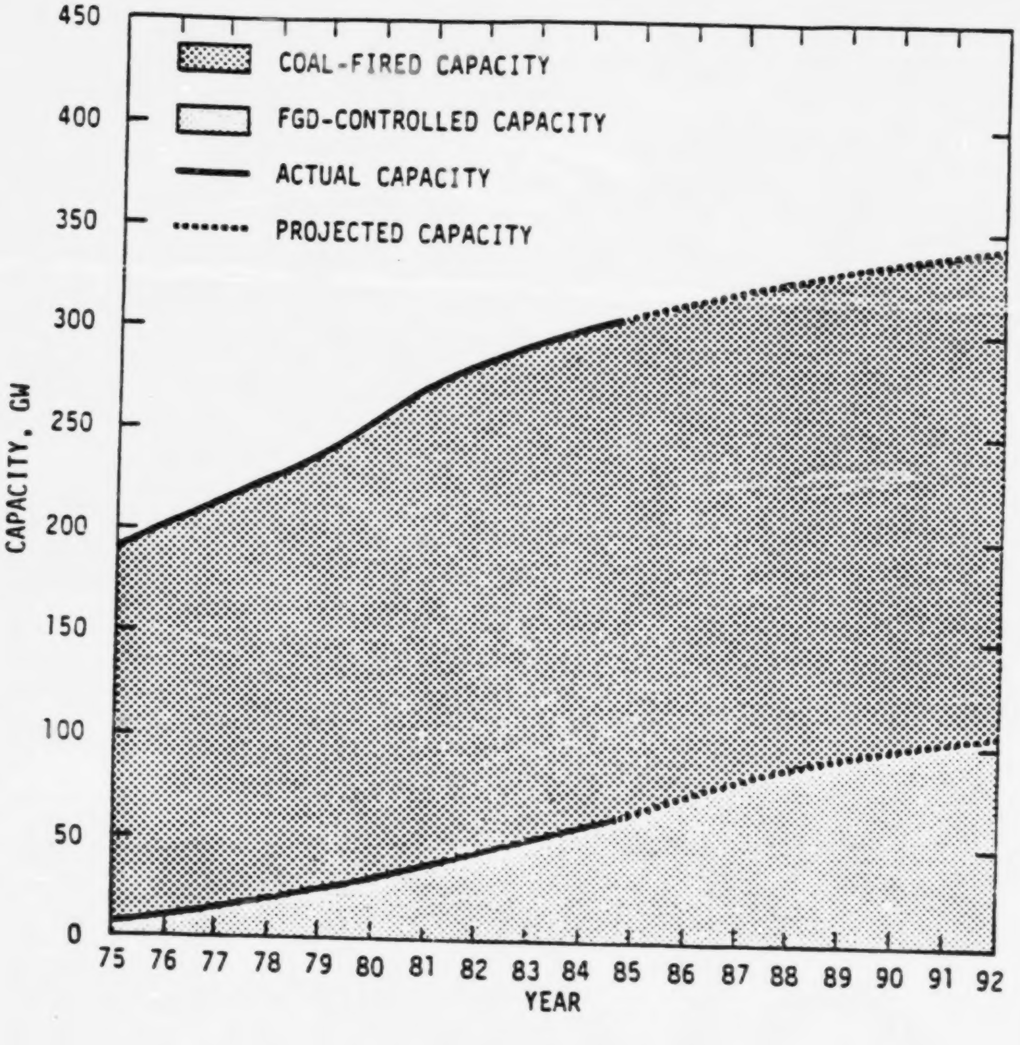


FIGURE 1 FGD AND COAL-FIRED CAPACITY

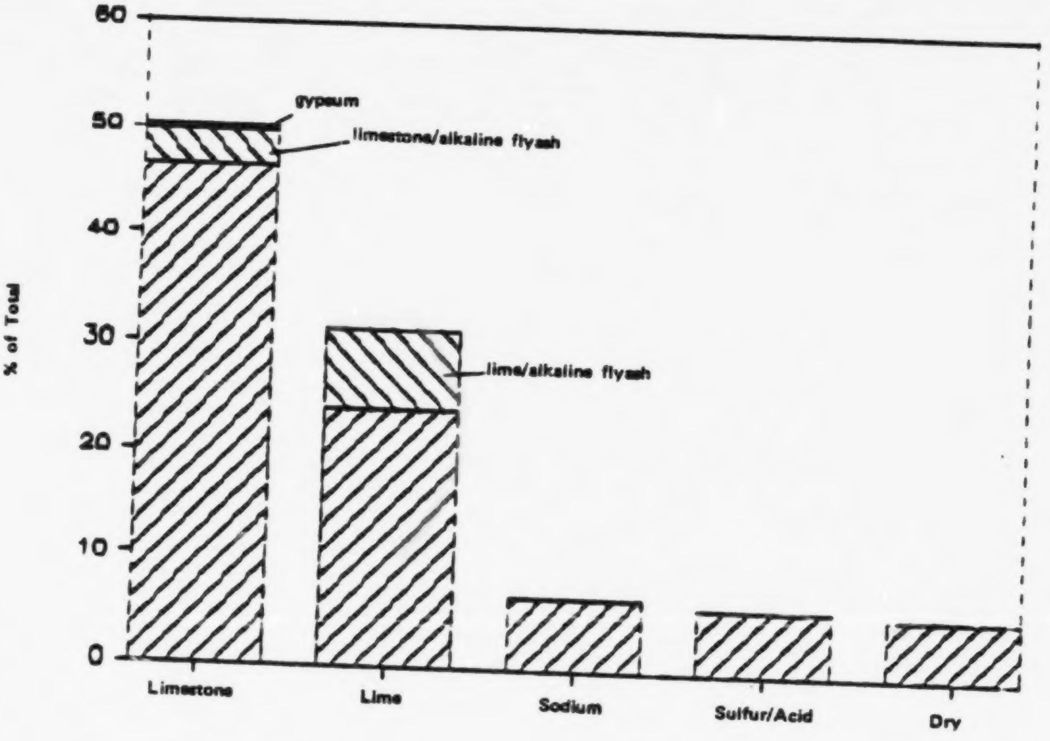


FIGURE 2 TYPES OF FGD SYSTEMS COMMITTED

SHORT TERM OUTLOOK

Table 1 is an alphabetical list of FGD systems which are in some stage of consideration ranging from projects where contracts are about to be awarded to systems associated with new boilers whose construction is highly questionable. It does not include major revisions or renovations of any existing FGD systems. This means the type of work done by Burns and McDonnell at Louisville Gas & Electric is not included. It does include both retrofits and new boiler FGD systems. In one case, the Zimmer plant, it includes a nuclear power plant being converted to coal. It does not include the cogeneration FGD systems.

FORECAST

The New Source Performance Standards were written under the concept that the most painless way to provide SO_2 removal was.by requiring only new plants to install scrubber systems. Therefore, the growth in scrubber systems is linked to the demand for new boilers which is in turn a function of replacement and expanding use of electricity. Nothing is as controversial as the question of future capacity and timing. NERC has made projections relatiye to peak load demand and concludes that the average growth rate per annum will be 2.5%.

The highest projected rate of growth for a NERC region is ERCOT, (Texas), with a growth rate of 4.0 percent/year, followed by SERC'S (Southeast) and SPP's (Southwest) growth of 2.9 and 2.7 percent, respectively. The lowest growth rates are projected for MAAC (Mid Atlantic) 1.3 percent and NPCC (Northeast) 1.7 percent. Growth for MAAP (North Central), is projected at 2.4 percent.

According to the 1984 NERC annual report, ERCOT systems expect approximately 20,000 MW of new generating capability to be added during the period 1984 through 1993. This total includes 10,344 MW of coal and lignite units, 4,800 MW of nuclear units, and 2,225 MW of cogeneration, with the remainder consisting of existing unit uprates and new units uncommitted as to fuel type. Retirements totaling 3,200 MW during the period are anticipated, resulting in a net addition of some 16,800 MW. Total electric energy production in ERCOT is forecast to increase 239,000 GHWh, almost 50%, during the next 10 years. The fuel mix will change substantially, according to system projections. Energy production by natural gas will drop to 35% of the total in 1993 (although the actual quantity of gas used will decrease by only 5%) and nuclear will contribute 11%. Coal and lignite fuel use will increase by 80%, to provide 53.5% of the total energy generated.

SPP members plan to increase generating capability 11,500 MW by 1993. Over the period SPP plans to retire some 73 generating units, as part of the plan to reduce oil and gas-fired capacity from 54.9% of total capacity to 43.6%. Coal-fired capacity will increase from the current 37.7% to 41.1% and nuclear capacity will increase from 2.8% to 9.8%. These plans are based on 1984 projections of 2.7% load growth per year. However, uncertainties concerning future load growth, coupled with financing constraints, may impact these plans. Reflecting this uncertainty, 12 out of 19 large coal/lignite plants scheduled for service by 1993 are only in the planning stages.

With an average annual increase in peak load demand nationwide of only 2% it would be necessary to add 15,000 MW of new capacity per year in order to maintain reserve margins at their present levels. However, because of the disparity in the growth rate in the various regions, the high growth regions will have to add more capacity sooner than the low growth regions. Burns and McDonnell has made some

TABLE 1 PLANNED FGD PROJECTS

Company Name/Unit Name	City	State	Capacity, MW (Gross)	Fuel % Sulfur	FGD Process
Arizona Public Service					
Cholla 5	Joseph City	Arizona	375	0.50	Process not selected
Atlantic City Electric					
Cumberland 1	Millville	New Jersey	330	3.25	Limestone
Basin Electric Power					
Antelope Valley 3	Beulah	North Dakota	560	0.68	Lime/spray drying
Boston Edison					
New Boston 1	Boston	Massachusetts	388	2.30	Limestone
New Boston 2	Boston	Massachusetts	388	2.30	Limestone
Central Maine Power					
Sears Island 1	Penobscot Bay	Maine	600	2.23	Process not selected
Cincinnati Gas & Electric					
East Bend 1	Rabbit Hash	Kentucky	650	4.00	Process not selected
Zimmer 1	Moscow	Ohio	1386	3.50	Process not selected
Cooperative Power					
N/D 1	Undecided	Ohio	750		Limestone
Delmarva Power & Light					
Vienna 9	Vienna	Maryland	550	2.50	Process not selected
Deseret Gen. and Trans.					
Bonanza 2	Vernal	Utah	410	0.50	Limestone
Florida Power & Light					
Martin 4	Martin County	Florida	800		Process not selected
Martin 4	Martin County	Florida	800		Process not selected
General Public Utilities					
Coal 1	Forked River	New Jersey	690	2.00	Limestone
Coal 2	Undecided	Undecided	690	3.50	Limestone
Indianapolis Power & Light					
Patriot 1	Patriot	Indiana	650	3.50	Limestone
Patriot 2	Patriot	Indiana	650	3.50	Limestone
Patriot 3	Patriot	Indiana	650	3.50	Limestone
Kentucky Utilities					
Hancock 2	Hawesville	Kentucky	708	3.50	Limestone
Louisville Gas & Electric					
Trimble County 1	Bedford	Kentucky	575	4.00	Process not selected
Trimble County 2	Bedford	Kentucky	575	4.00	Process not selected
Lower Colorado River Authority					
Fayette Power Project 4	La Grange	Texas	451	1.70	Limestone
Nebraska Public Power District					
Fossil III 1	Sargent	Nebraska	650	0.36	Process not selected

TABLE 1 PLANNED FGD PROJECTS (Continued)

Company Name/Unit Name	City	State	Capacity, MW (Gross)	Fuel % Sulfur	FGD Process
Nevada Power					
Harry Allen 1	Las Vegas	Nevada	500		Process not selected
Harry Allen 2	Las Vegas	Nevada	500		Process not selected
Harry Allen 3	Las Vegas	Nevada	500		Process not selected
Harry Allen 4	Las Vegas	Nevada	500		Process not selected
Public Service of New Mexico					
New Mexico 1	Bisti	New Mexico	500		Process not selected
Public Service of Colorado					
Pawnee 2	Rush	Colorado	500	0.35	Trona/dry injection
Salt River Project					
Coronado 3	St. Johns	Arizona	400	0.60	Limestone
San Antonio Public Service					
N/D 1	Undecided	Texas	500	1.50	Limestone
N/D 2	Undecided	Texas	500	1.50	Limestone
N/D 3	Undecided	Texas	500	1.50	Limestone
N/D 4	Undecided	Texas	500	1.50	Limestone
Seminole Electric					
Taylor 1	Perry	Florida	620		Process not selected
Taylor 2	Perry	Florida	620		Process not selected
Sierra Pacific Power					
Thousand Springs 1	Wells	Nevada	500		Process not selected
Thousand Springs 2	Wells	Nevada	500		Process not selected
Thousand Springs 3	Wells	Nevada	500		Process not selected
Southwestern Electric Power					
Walker Co. 1	Huntsville	Texas	720	1.49	Process not selected
Walker Co. 2	Huntsville	Texas	720	1.49	Process not selected
Southwestern Public Service					
South Plains	Idalo	Texas	572		Process not selected
Tucson Electric Power					
Springerville 3	Springerville	Arizona	370	0.61	Process not selected
Washington Water Power					
Creston Coal 1	Creston	Washington	570		Limestone
Creston Coal 2	Creston	Washington	570		Limestone
Creston Coal 3	Creston	Washington	570		Limestone
Creston Coal 4	Creston	Washington	570		Limestone
West Texas Utilities					
Oklaunion 2	Oklaunion	Texas	720	0.34	Process not selected
White Pine County					
White Pine Power Project 1	Ely	Nevada	820	0.60	Process not selected
White Pine Power Project 2	Ely	Nevada	820	0.60	Process not selected

projections assuming that new capacity will have to be added when projected reserve margins dip below 20%. They have concluded that for the entire nation, unplanned new capacity requirements through 1998 total 47,535 MW. ERCOT and SERC show the greatest requirements: approximately 15,000 MW. MAAC and NPCC still will have sufficient capacity in 1998.

In order to maintain a 20% reserve margin and assuming a six year construction schedule ERCOT and MAPP have to start new coal fired projects now. SPP, MAIN, and SERC would need to begin by 1988 or 1989.

In addition to new plants to provide additional capacity there is a need for replacement. There is a strong present emphasis on life extension. The average boiler today is ancient by previous standards. But even if plant life is extended to 60 years there is an annual replacement requirement of 10,000 MW. Over the last few years utilities have started almost no new projects and in fact a number of nuclear projects have been cancelled. This low level of activity has a cumulative effect and must eventually be countered with accelerated activity.

The consequence we see is an unusually high level of new boiler construction in the 1990's. These projections are shown in Figure 3. Installed capacity increases at a modest rate until the early 1990's but sometime in the late 1990's the installed FGD capacity would reach 175,000 MW.

Our projections show that a substantial percentage of the new construction will involve spray dryer FGD systems as opposed to wet systems. This is because of the substantial amount of western low sulfur coal that will be burned in new boilers. Our assumptions are based on wet systems being used for high sulfur coal and dry systems used for low sulfur coal. As can be seen from Figure 3 nearly 40,000 MW of spray dryer systems will be on line by the late 1990's. The above projections are based on new boiler FGD construction only and retrofits that are already planned. They do not take into account major acid rain legislation.

ACID RAIN

The effect of acid rain control on the FGD market will be a function of the domestic political situation, the international political situation and to a minor extent on additional scientific findings. On the international political scene, the United States has slipped from a leading position to one in which it, along with the United Kingdom, may be among the few developed countries not proceeding with a full program. Japan has led with the most stringent controls. West Germany has recently enacted sweeping legislation that requires all major power plants to reduce emissions to 400 mg/m^3. Depending on the coal type this would be the equivalent in most U.S. plants of the 95% SO_2 removal. German utilities responded to the 1983 legislation by an accelerated purchase program of SO_2 systems. Engineering or firm orders have been let for over 35,000 MW of new systems in this period. Final design and construction is also proceeding on an accelerated rate.

Other European countries have joined the 30% club, so-called because member countries commit themselves to cut annual sulfur emissions 30 percent from their 1980 base emission levels by 1993 at the latest. The first countries to join the "30% Club" were Austria, Canada, Denmark, Finland, France, West Germany, the Netherlands, Norway, Sweden, and Switzerland. Belgium, Belorussia (a part of the USSR), Bulgaria, Czechoslovakia, East Germany, Italy, Liechtenstein, Luxembourg, the Ukraine, and the USSR joined later.

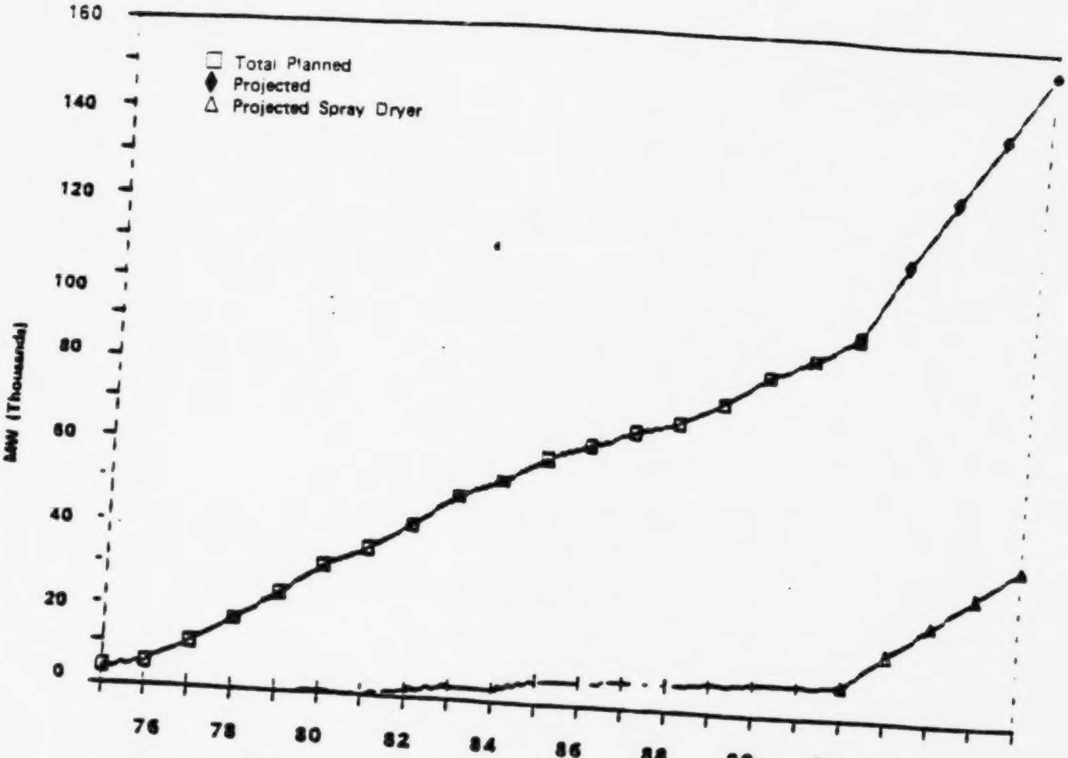


FIGURE 3 PROJECTED ON-LINE FGD SYSTEMS WITH SPRAY DRYER SEGMENT

Individual members of Congress appear to be favorable towards acid rain legislation. However, the administration is opposed to the immediate mandate of scrubber systems. It does not appear that there will be legislation in the immediate future. However, there are a number of bills before Congress.

Sen. Robert T. Stafford (R-VT) introduced the "Acid Rain Control Act of 1985". The bill proposes a 10 million ton reduction in sulfur dioxide emissions in the 31 states east of the Mississippi River. The reduction would take place over a 10-year period and would be calculated from 1980 sulfur dioxide emission levels. Sen. George Mitchell (D-ME) introduced bill S.283 which is identical to the measure (S.145) he introduced in the 98th Congress and would require a 10 million ton reduction of sulfur dioxide (SO_2) emissions within 10 years of enactment. Pollution sources that achieve sulfur reductions through fuel switching would have six years after enactment to achieve those reductions, while sources that use technological controls would have 10 years to comply.

In the House, Rep. Conte introduced H.R.1030 which would require a reduction of 12 million tons of SO_2 emissions and 4 million tons of nitrogen oxide emissions in two phases over a 13-year period. The bill provides partial cost sharing through a 1.5 mil-per-kilowatt-hour tax on electricity generated in the lower 48 states except for hydropower and nuclear. In the first phase, a 6.5 million ton reduction of SO_2 would require the 50 highest emitting power plants to install scrubbers. In the second phase, States would decide how to achieve the remaining 5.5 million ton reduction.

Senator Proxmire's proposal would require a 10 million ton SO_2 reduction over 13 years in the 31 states east of the Mississippi River. Reductions would be divided into two phases of six and four years, respectively, with a three-year period between for evaluation of an accelerated acid rain research program conducted during the first phase. The bill would allow utilities to use cheaper control methods such as coal washing and fuel switching during the first phase, and would require more expensive controls during the second phase.

It is possible that a significant number of FGD systems could be required by the individual states in the absence of a federal acid rain control program. The states already actively in pursuit of this end include New York, Massachusetts, Maine, New Hampshire, Vermont, California, Minnesota and Wisconsin.

In addition to the confusing political factors, there is the possiblity of new evidence on the effects of acid rain. The research program generated by the President's approach could either reinforce the need for FGD systems or provide ammunition for the opponents of an acid rain control program.

With all these factors involved it is difficult to predict the course of acid rain legislation. Instead we have charted in Figure 4 the maximum and minimum effects. On the assumption that no legislation is imminent it is unlikely that any systems would actually be in operation until 1992. Under the most ambitious programs it is unlikely that more than 60,000 MW systems would be mandated. The shortest time span for implementation in the various proposals would be 5 years. The top line in the graph compresses 60,000 additional MW of FGD systems in the 1992-1996 time frame or 12,000 MW per year. The middle line shows the maximum number of megawatts distributed over a 13 year time frame. This would be 4600 MW a year beginning in 1992 and by 1996 would have added 23,000 MW totally to the FGD system base. The bottom line shows FGD systems operating without any acid rain control legislation.

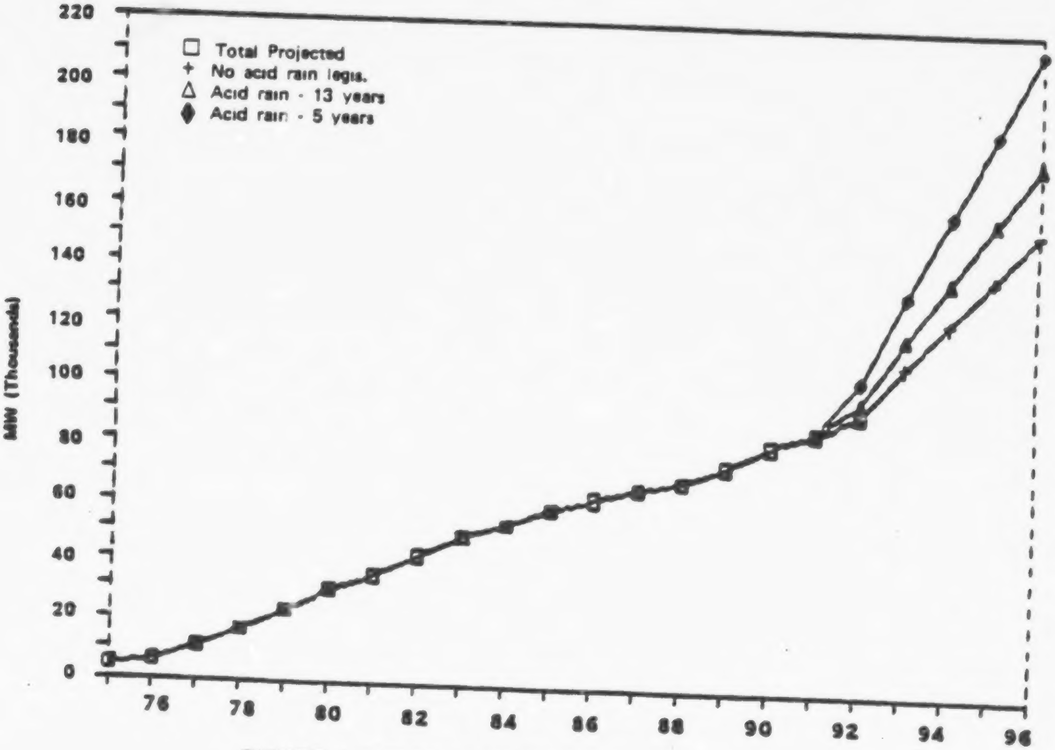


FIGURE 4 FGD PROJECTIONS INCLUDING ACID RAIN

When put in this perspective it is apparent that acid rain is likely to have less effect in any one year than either the peak load demand increase or changes in the replacement rate for older boilers. There is another consideration in determining the impact of acid rain control. That is any acid rain legislation is interrelated to decisions relative to new boiler construction. If faced with retrofitting old plants with scrubbers, utilities might opt to retire the plants at an earlier date than otherwise anticipated.

REPAIR PART AND SERVICE MARKET

The commercial FGD market has too often been viewed in terms of the initial supply of equipment and services. The scrubber company is most frequently a supplier of a complete system. However it purchases most of the components. In fact even the components which it designs are most frequently fabricated by others. After the system is installed, repair parts for components are typically purchased directly from the components supplier. (The process designer supplies the user with adequate parts data so that he can easily order from the original component supplier.)

The market for items such as gaskets which are replaced each year is substantial. The gasket supplier is dealing with the whole system base of 50,000 MW and not with the few thousand MW that may be purchased in any one year. Many other components in the system are replaced frequently. Rotating parts in pumps, fans, valves and parts exposed to abrasive slurries are frequently replaced and have generated a repair part business which provides significant profit for a number of companies.

We estimate that the total replacement part business for FGD systems in 1985 will be between $160 and $170 million. This market will double by the middle 1990's and will continue to expand rapidly until all coal-fired boilers are fitted with FGD systems.

The market for individual components is substantial when one considers the initial purchases plus the repair parts for a given year. One of the largest single items is baghouses associated with spray dryer systems. By 1991 purchases of fabric filters (baghouses) could exceed $250 million per annum. Ducting is estimated to exceed $200 million per year. Spray dryer purchases are estimated to exceed $160 million. Purchases of dampers are estimated at nearly $90 million per annum by 1991. Sales of pumps and pump components should exceed $45 million by that year.

Engineering and maintenance services are another major commercial area. Older FGD systems will be updated. The first major example is at Louisville Gas and Electric where a number of systems have been overhauled by Burns and McDonnell. Some maintenance services are furnished by the original scrubber system supplier. Others are furnished by manufacturers of components. For instance, a utility can arrange for periodic audits of its continuous emissions monitoring equipment (CEM's) with the CEM manufacturer or third party testing services.

Another major area involves the supply of material. The largest such example is limestone. FGD systems represent a substantial limestone market. The impact of the flue gas desulfurization market on the limestone industry has been equal to its impact on the air pollution control industry.

COMMERCIAL TRENDS

The flue gas desulfurization industry is maturing and has become an accepted part of the utility scene. Some of industry trends are not surprising. Integration is typical of a maturing industry. The large are getting larger. Combustion Engineering which has been strong in wet systems has purchased Rockwell International dry technology. Rockwell International was a pioneer in spray dryer scrubbing. Thermo Electron, a major supplier of emission monitoring equipment, has purchased the monitoring group of another major supplier, Contraves. Wheelabrator is now a part of the Signal Corporation so that UOP and Wheelabrator are now part of the same group along with M.W. Kellogg, therefore, effectively combining three former competitors. Flakt has purchased the air pollution control group of Carborundum thus combining two former suppliers of dry FGD systems.

Internationalization will continue at a rapid pace. A sudden burst of activity in West Germany has benefited the global FGD suppliers. Research-Cottrell, General Electric Environmental Services, Niro-Atomizer, and Flakt were able to bring some of their U.S. talent to bear on the sudden bonanza. Likewise companies such as Saarberg-Holter and Deutsche Babcock which have not made their presence felt in the U.S. market are likely to come on stronger in the future based on their success and experience in the West German market. The same is true of several Japanese companies who have benefited through license or partnership activities in Europe.

Successful development gives the competitive edge to vendor companies. Companies which are approaching the market on a global basis can afford to spend more on research and development and are therefore more likely to succeed. The same is true of component suppliers. Lechler and Euroform are examples of two companies which have been equally successful in both the U.S. and Europe. Lechler through its U.S. subsidiary Spraco, is a major manufacturer of nozzles whereas Euroform through Munters in the U.S. is a major manufacturer of mist eliminators. At the present time there are not many other successful examples of international component suppliers. This situation is very likely to change in the next decade.

The U.S. is not a large enough percentage of the world market to allow companies to concentrate solely on the U.S. and ignore the rest of the world. Figure 5 shows the world air pollution control industry sales as based on 1984 orders and 1985 projections. Because of the large German market, FGD sales worldwide have climbed enormously. FGD systems represent a much larger portion of the total world air pollution control market than either precipitators or fabric filters. However, in combination there is still more money spent on particulate control than on FGD. Figure 6 indicates the expanded size of the European market this year. It is nearly as large as the rest of the world combined. This is the reverse of the situation a few years ago when the U.S. was the big market. A few years prior to the U.S dominance the Japanese market was the largest market. For the truly international supplier, the FGD business has been relatively steady. It is only in the individual countries where the demand has flunctuated wildly.

Another trend is a stronger role for the component supplier. As the number of systems in place keeps growing the ratio of repair parts sales to new component sales grows. Component suppliers have the incentive to spend more money on research and development. They also obtain unique experience with their involvement with a plant from startup throughout its operating life.

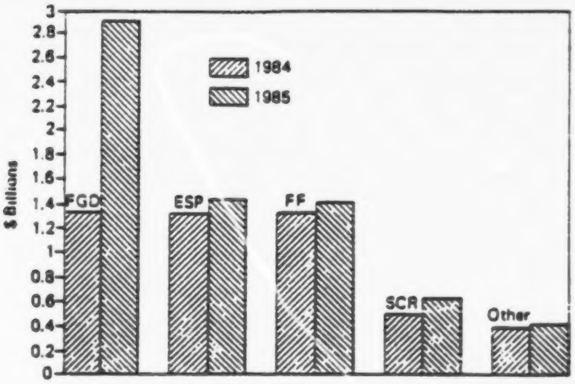


FIGURE 5 WORLD AIR POLLUTION CONTROL
MARKET BY TYPE, 1984 VS. 1985
PROJECTIONS

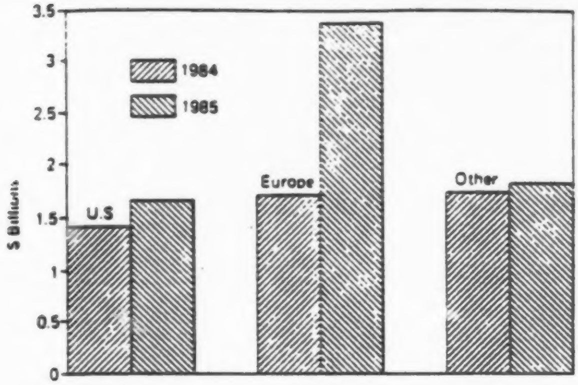


FIGURE 6 WORLD AIR POLLUTION CONTROL
EQUIPMENT, 1984 VS. 1985
PROJECTIONS (COMPLETE SYSTEMS)

Despite an expanding role for architect engineers and for component suppliers, we expect the process design companies to maintain the leading role in supplying flue gas desulfurization systems. The scrubber system supplier not only acts to integrate all the components, but he is an insurance agent. By guaranteeing the system he eliminates an element of risk which few utilities are willing to take on their own. We believe that the scrubber system companies will survive not only the onslaught of architect engineers and component suppliers but of the boiler companies as well. We recently analyzed the orders for new boilers and the orders for scrubber systems. The boiler companies with FGD systems were not noticeably more effective in selling FGD systems with their own new boilers than they were in selling FGD systems in general. The conclusion, therefore, is that the boiler companies have been successful in selling FGD systems because they make a competitive FGD product and not just because they are boiler manufacturers. It can also be concluded that there is no monopolistic opportunity and that utilities and architect engineers will continue to look at separate contracts for boilers and scrubber systems.

CONCLUSION:

Even with modest increases in peak load demand a large number of new boilers will be required in the 1990's. The favorite fuel is almost certain to be coal and this will result in purchases of substantial numbers of FGD systems. The impact of load growth and replacement is greater than acid rain legislation in determining the actual quantity of systems which will be purchased. The commercial environment of the industry will change as internationalization and integration continue. New technology will be a major factor. Just as the advent of spray dryer technology completely changed the competitive positions in the industry, a variety of promising new technologies could in the future have the same impact.

REFERENCES

1. North American Electric Reliability Council Annual Report 1984.
2. Electrical World, January 1985
   "Capacity Additions How Much, How Soon? by H.A. Cavanaugh
3. U.S. Flue Gas Desulfurization 1984-1994, The McIlvaine Co.
4. FGD Newsletter, The McIlvaine Co.
5. FGD Manual, The McIlvaine Co.
6. Journal of Air Pollution Control Association, March 1985, "1985 Air Pollution Control Market Forecast" by Robert W. McIlvaine
7. Project Summary Utility FGD Survey, October 1983-September 1984, EPRI

SURVEY REPORT AND ASSESSMENT OF UTILITY FLUE GAS DESULFURIZATION SYSTEM INSTALLATIONS IN EUROPE

by: William Ellison
Ellison Consultants
Monrovia, Maryland 21770-9316

ABSTRACT

This paper presents details of recent surveys of major programs for flue gas desulfurization (FGD) and NO_x removal installation in West Germany. The purpose of the paper is to provide an understanding of the principal types of control system designs that are being applied, to outline technological advancements that are being achieved, and to describe operating experience gained to date in expanded use of FGD and selective catalytic reduction (SCR) in Europe in the 1980s. Significant differences from FGD and NO_x removal practice in U.S.A. and Japan are reviewed and specific information that may serve to help improve operation and reliability of new and retrofit installations in U.S.A. is offered.

WEST GERMAN SO_2 REGULATIONS

Recent surveys have indicated that approximately 50% of the forested areas had been damaged, and acid rain is viewed as a significant cause. In 1983 West Germany enacted a major national acid rain control directive (1), subsequently tightened in 1984, that has led to a major program of FGD installation, primarily on large coal-fired boilers. Units larger than 110 MW(e) have been required to clean up by 1988 or phase out by 1993. Control of emissions from smaller boilers is tied to a 1993 deadline. Table 1 shows the number and size of existing boilers, almost all firing low/medium sulfur fuel, generally bituminous coal or lignite, and indicates that more than 150 units are impacted by the 1988 SO_2-control requirements. Also affected are 7,400 MW(e) of new, coal-burning units (2) under construction or expected to start up by approximately 1990. Table 2 shows the specified level of control of emissions, with 85% SO_2 removal required for units larger than 110 MW(e) regardless of fuel sulfur level, and with 60% removal specified for the large industrial boilers, i.e. 35 to 110 MW(e) size, deadlined for 1993.

FGD UTILIZATION

In keeping with the 1988 target compliance-date almost all utility units are being retrofitted with scrubbers except for approximately 12,000 MW(e) of capacity that by 1984 owner-declaration are to be retired by 1993 after no more than 30,000 additional hours of operation. Table 3 summarizes commercial FGD activity to date, with over 100 FGD installations, primarily commercial-gypsum-producing types, to be erected, comprising 30,000 MW(e). Approximately 50,000 MW(e) of FGD is expected to be in place by the early 1990s (3). Those FGD facilities already running are the result of a comparatively modest control program that began prior to 1983 under the jurisdiction of individual state governments that resulted in twenty FGD commitments, almost all for slip-stream single-module installations. Comparatively few boilers under 110 MW(e) have been retrofitted with FGD to date. Influenced by the new control activity in Germany, approximately 2000 MW(e) of usable-gypsum-producing FGD systems are being installed in The Netherlands, and a major FGD program is under way in Austria on utility boilers.

PRINCIPAL FGD TECHNOLOGY USED

Table 4 quantifies the lime/limestone FGD market that has been shared by the six principal system suppliers, a mix of Japanese, U.S. and German processes (2). FGD selection has reflected a strong emphasis in Germany on the need to achieve high system availability. Procurement is commonly predicated on a guaranteed system availability of 95%. As in Japan, most of the installations of each principal supplier are designed to employ forced oxidation to yield a commercially usable gypsum and to thus avoid the substantial cost and complexity of alternative throwaway-waste management. However, a total of 30 throwaway waste FGD systems comprising 9000 MW(e) are being installed, all at minemouth lignite-fired plants where disposal of solid waste in the mine is anticipated. Reheating of stack gas to a minimum of 72°C (162°F) at the stack exit is required by code, and rotary regenerative heat exchangers are being commonly used for this purpose. Gypsum-solids dewatering systems are comparatively simple, typically comprising primary dewatering by liquid cyclones, with final dewatering by centrifuge or horizontal vacuum filter. Due to transportation-economics a substantial proportion of installations in Germany use lime in lieu of limestone. However, as a national energy conservation measure, all recent FGD commitments have been dedicated to use of limestone reagent. The largest single share of the FGD market, over 8000 MW(e), has applied a magnesia-buffered $CaSO_4$-unsaturated lime-scrubbing process (adapted in latest installations to use of limestone.) $CaSO_4$-unsaturated design is a familiar mode of operation in U.S.A. but one not commonly coupled here with forced-oxidation design. Unsaturated mode installations in U.S.A. have had a uniquely high level of availability on difficult high-sulfur applications here (4).

KAWASAKI MAGNESIA GYPSUM

This most frequently applied FGD process uses a two-stage limestone spray tower followed by post-reaction incorporating forced oxidation in the sump. In initial installations, magnesia additive enhances SO_2 absorption and internal scale control, and pH control in the forced oxidation step is achieved with sulfuric acid reagent feed. Latest installations instead achieve forced oxidation at the low pH in the bottom of the absorber.

MITSUBISHI LIME/LIMESTONE

The conservatively designed Mitsubishi Process, the most commonly used in Japan, employs separate equipment components for gas quenching (chloride removal), spray absorption/reaction, and forced oxidation, pH-controlled by sulfuric acid reagent feed.

CHEMICO-MITSUI

Initial installations have included Chemico (GEESI) spray-tower absorbers and use of the Mitsui forced-oxidation system from Japan. Subsequent installations in Germany have incorporated the oxidation step in the bottom of the absorber tower as in the case of applications of the process in U.S.A.

RESEARCH COTTRELL DOUBLE-LOOP

Research Cottrell's familiar double loop limestone scrubbing process used in Germany has been the principal forced-oxidation FGD process applied in the U.S., and accounts for almost all usable-gypsum producing FGD installations in operation or under construction here. With large scale use of by-product gypsum in Germany for plaster/mortar products, Research Cottrell installations there include provision for advantageous drying of the cake product by direct contact with a portion of the scrubber inlet-gas stream.

SAARBERG-HOELTER BUFFERED CLEAR LIQUOR

This German process employing formic acid buffering uses low-suspended-solids thickener-overflow liquor for SO_2 absorption in a unique scrubber comprising multiple downflow-ducts equipped with co-current sprays followed by a counterflow section, and with forced-oxidation performed in the sump of the scrubber. Scrubbing liquid thereafter flows to a neutralization tank for lime addition before discharge to the thickener. In at least one installation this supplier is using the plant cooling tower structure in lieu of a flue-gas stack to discharge the FGD outlet gas without need for reheat.

BISCHOFF SINGLE-LOOP

German supplier, Gottfried Bischoff, with a substantial background in supply of large-capacity wet-scrubbers for the iron and steel industry in the 1960s, has supplied a number of comparatively simple, single-module, approximately 200 ft. high by 40 ft. diameter, spray towers of over 400 MW(e) capacity designed to also incorporate the forced-oxidation and lime/limestone reaction steps. An initial installation on the North Sea uses seawater for FGD makeup water yet yields a usable gypsum by adequate fresh-water washing.

OTHER FGD PROCESSES

Table 5 summarizes commitments to specialized FGD processes.

WELLMAN LORD

The familiar Wellman Lord process has been applied in several instances, primarily for elemental sulfur by-product yield.

WALTHER AMMONIA

In four installations the Walther Process uses two stages of ammonia scrubbing to produce ammonium sulfate by-product liquor that is converted to a dry fertilizer product in a small auxiliary spray-dryer system. At least one of the installlations is designed for simultaneous removal of NO_x.

ACTIVATED CARBON

A Berbau Forschung installation will use activated carbon for SO_2 adsorption and high-temperature regeneration to produce a rich-SO_2 off-gas that will be converted into commercial sulfuric acid. The adsorber also collects NO_x. The carbon is slowly cycled between the adsorber and regenerator by a closed conveyor system.

DRY SCRUBBING

A number of small boilers are being equipped with common throwaway-waste dry scrubbing systems. This technique may be expected to be applied to additional boilers of size 110 MW(e) and less in meeting a 1993 deadline for 60% SO_2 removal.

LIMB

While not yet installed on a commercial scale, use of lime/limestone injection in conjunction with low-NO_x burners has been developed for lignite firing and is being tested/demonstrated on bituminous coal firing.

Like dry scrubbing it may be applied on some boilers of 110 MW(e) capacity and less to meet 60% SO_2 removal requirements by 1993. Such means of low efficiency, combined SO_2/NO_x emission control can be expected to be advantageous on large industrial boilers.

DISCUSSION OF SO_2 CONTROL ACTIVITIES

MAJOR TECHNICAL PROBLEMS

Operating with characteristically low or moderate coal sulfur level, and applying commercially demonstrated and conservatively designed forced-oxidation systems, no critical technical problems have been experienced or forecast at the present time. Feasibility of regenerative flue-gas reheat using rotary regenerative heat exchangers has been effectively demonstrated. Great attention is being given to means of ensuring commercial utilization of more than 3 million annual tons of anticipated FGD gypsum production. New technologies are developed and are being promoted for reprocessing some of the by-product to anhydrite and alpha hemihydrate forms so as to supply available markets beyond those for normal gypsum alone. Through wastewater purge treatment carried out in the presence of gypsum precipitation from $CaSO_4$-supersaturated liquid, very low trace metal concentrations are achieved prior to outfall discharge. Unlike Japan, German boilers are typically inland on fresh water streams and do not have seawater receiving-bodies to which to discharge FGD chloride-liquor blowdown from usable-gypsum-producing FGD operation. Due to the significant potential impact of the chloride blowdown on German rivers a major policy decision by the national government is pending on acceptable long-term means of FGD-chloride-waste management.

OPERATING EXPERIENCE

The many single-module slip-stream FGD system installations already in operation are understood to have provided acceptable reliability and performance. However, German electric utility specialists note that these earliest installations have not been subjected to typical full-scale electric-utility-industry operating conditions requiring high availability at sustained high/variable load. Thus, Germany's massive FGD program is at too early a stage of implementation to show broadly demonstrated success or to thoroughly characterize performance and reliability of system designs that are being applied.

WEST GERMAN NO_x CONTROL ACTIVITY

NEW REGULATIONS

Although mobile sources account for more than 80% of the NO_x emission inventory, national rules as amended in 1984, (Table 6), call for 200 mg NO_2/Nm^3, i.e. approximately 100 ppm, for the large utility boilers (5). However, old boilers of approximately 12,000 MW(e) aggregate capacity to be phased out, i.e. retired no later than 1993 after no more than 30,000 additional hour of operation,are allowed 650mg NO_2/Nm^3. The great stringency of the large-boiler NO_x emission limit is illustrated in Table 7 by comparison with nationwide requirements in U.S.A. and Japan. Additional regulations are pending in West Germany that will require lead-free fuel and catalytic converters for gasoline-fueled automobiles. Significant NO_x control legislation has also passed or is pending in Austria, Switzerland, The Netherlands, Denmark, Sweden and the European Economic Community.

MEANS OF CONTROL

Commercially developed combustion modifications for NO_x control are expected to be routinely applied, primarily on dry-bottom boilers. However, the very substantial reduction that will be required from the uncontrolled NO_x emission levels illustrated by Table 8 is expected to result in widespread application of selective catalytic reduction to many German utility boilers larger than 110 MW(e).

SCR ACTIVITY

Due to concerns about applicability at electric utility plants in West Germany of extensive commercial SCR experience in Japan, over 50 SCR pilot-plant trains are being installed and tested (Table 9) to assess catalyst performance and characteristics. Extensive SCR field pilot-scale investigation is taking place because German boilers to be retrofitted with SCR are considered to have a more variable load pattern than those in Japan that have been equipped and operated with SCR. Also, due to specific local regulations in some German states, a 90% SCR-efficiency requirement, uncommon and generally avoided in Japan, is being specified in a number of applications. As per Table 9, 26 specific commercial installations are already forecast, several of which will be applied downstream of FGD because of inadequate plot space to permit normal tie in of the SCR reactor upstream of the boiler air heater. In some states such as Baden-Wuerttemberg, the most heavily forest-damaged area, and Nordrhein-Westfalia, the greatest emitting area, state-administered NO_x control planning is more advanced than in others. In Baden-Wuerttemberg, 3700 MW(e) of SCR will be in place by 1990. Of 9 SCR system suppliers, 6 are licensees of Japanese processes while 3 offer German developments including use of activated carbon or a ceramic molecular sieve. The first major SCR facility is being installed on a 460 MW(e) bituminous-coal-fired, dry bottom boiler and will begin operation by early 1986. Another installation of 170 MW(e) capacity will be completed about the same time on a bituminous-coal-fired, wet bottom boiler and will achieve 90% NO_x removal.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and

therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

REFERENCES

1. Federal Republic of Germany, Thirteenth order implementing the federal emission control act (large furnaces order) - 13th BImSchV, cabinet decision of 14 June 1983.
2. REA fur 33,000 MW(FGD for 33,000 MW), Energie, Volume 36, Number 12, December 1984.
3. Davids, P., Haug, N., Lange, M., Oels, H.-J., and Schmidt, B, (UBA/Berlin). Luftreinhaltung bei kraftwerks und industriefeuerungen. BWK, Volume 37, Number 4, April 1985.
4. Ellison, W. Experience with wet lime/limestone FGD systems. Paper presented at Second International Conference on Acid Rain -- Regulatory Aspects and Engineering Solutions, Washington, D.C. March 26-27, 1985.
5. Lange, M., (UBA/Berlin). Regulations for fulfillment of requirements for NO_x emission restrictions in large furnace systems in Europe. 1985.

TABLE 1. POPULATION OF EXISTING WEST GERMAN COAL AND OIL FIRED BOILERS

Size, MW(e)	Number	Aggregate MW(e)	Average MW(e)
Over 300	41	18,400	450
135-300	91	17,800	195
75-135	95	9,900	104
30-75	378	18,500	49
9-30	548	10,600	19
Over 9	1153 (Tot.)	75,200 (Tot.)	65

TABLE 2. FEDERAL SO_2 CONTROL REQUIREMENTS FOR WEST GERMAN COAL-FIRED BOILERS

	Emission limit			
Size MW(e)	mg/Nm^3 (Ap. lb/MMBtu)	% removal	Deadline	Ap.No. existing
Over 110	400 (0.5Avg.)	85	7/1/88	160
35 to 110	2,000 (2.5Avg.)	60	4/1/93	370
18 to 35	2,000 (2.5Avg.)	-	4/1/93	300

TABLE 3. FGD COMMITMENTS IN WEST GERMANY (END OF 1984)

Status	Aggregate MW(e)	No. of Install.	Average MW(e)
In operation	4,700	13	360
Purchased but not in operation	29,800	102	290
Total	34,500	115	300

TABLE 4. PRINCIPAL PROCESSES USED

Process	Aggregate MW(e)	No. of Install.	Average MW(e)
Kawasaki Magnesia Gypsum	8,200	27	300
Mitsubishi Lime/Limestone	4,600	16	290
Chemico-Mitsui (GEESI)	5,600	15	370
Research Cottrell Double-Loop	3,600	9	400
Saarberg-Hoelter Buff.Clear Liq.	5,500	21	260
Bischoff Single-Loop	3,700	17	220
Total	31,200	105	300

TABLE 5. SPECIAL PROCESSES USED

Process	Aggregate MW(e)	No. of Install.	Average MW(e)
Wellman Lord	1,400	3	470
Walther Ammonia	750	4	190
Activated Carbon	230	1	230
Dry scrubbing	320	6	50
Total	2,700	14	190

TABLE 6. 1988 FEDERAL NO_x CONTROL REQUIREMENTS FOR WEST GERMAN COAL-FIRED BOILERS

	Emission limit, mg as NO_2/Nm^3 (6% O_2)		
		Existing	
Size MW(e)	New	High Ca.Fact	Low Cap. Fact **
Over 110	200	200	650*
35 to 110	400	650*	650*
18 to 35	400	650*	650*

* 1,300 (5% O_2) for wet bottom boilers

** Less than 30,000 hours remaining service life

TABLE 7. COMPARISON OF NO_x EMISSION STANDARDS FOR COAL-FIRED BOILERS

Country	National NO_x emission standard. mg as NO_2/Nm^3 (6% O_2)
West Germany. new and existing over 110 MW(e), 1/2 Hr. ave.	200
U.S.A.. new, over 25 MW(e)	600-750
Japan	410-615

TABLE 8. TYPICAL PRE-CONTROL BOILER NO_x EMISSIONS

Type boiler	Emission, mg as NO_2/Nm^3 (6% O_2)	
	Range	Mean
Bituminous, wet bottom	800-2,800	1,700
Bituminous, dry bottom	800-1,500	1,200
Lignite, tangentially fired	400-700	500

TABLE 9. SCR FOR COAL-FIRED BOILERS

Position of SCR	No. pilot plant trains, 100-10,000 m^3/h	No. (MWe) commercial installations* planned or in construction
Upstream air heater	39	23 (6,200)
Downstream FGD	12	3 (420)

* Installation startup 1986 to 1989

Recent Developments in SO_2 and NO_x Abatement Technology in Japan

by: Jumpei Ando
Chuo University
Tokyo, Japan

ABSTRACT

More than 1,400 FGD plants have been constructed in Japan with a total capacity of treating 130,000,000 Nm^3/h of flue gas (43,000 MW equivalent). Thirty FGD plants have been operated treating about 90% of total flue gas from coal-fired utility boilers. All of the FGD plants for coal by-produce salable gypsum. On the other hand, the total capacity of selective catalytic reduction (SCR) of NO_x exceeded 90,000,000 Nm^3/h (30,000 MW). Twenty coal-fired boilers use SCR in addition to FGD. All of the FGD and SCR plants have been operated with over 99% reliability. The investment cost for limestone/gypsum process FGD plants for coal-fired boilers has been lowered from about 30,000 yen/kW* in 1979-1980 to about 20,000 yen/kW in 1983-1984. The power consumption of the FGD processes was also reduced from 2.1-2.6% to 1.7-2.1%. The annualized cost of the wet limestone/gypsum process is currently about 1.4 yen/kWh including 7 years depreciation and 10% interest. The investment cost of SCR for coal-fired utility boilers is about 6,000 yen/kW, while the annualized SCR cost is 0.5-0.6 yen/kWh including 7 years depreciation and 10% interest. For the removal of acid (H^+), NO_x abatement by combustion modification (CM) is the most economical, while SCR is more costly. There have been no significant developments in simultaneous SO_2 and NO_x removal technology except that two test plants have been operated with activated carbon processes. Several industrial coal-fired boilers using fluidized-bed combustion have been put into operation, reducing both SO_2 and NO_x.

ENERGY SUPPLY AND AIR POLLUTION CONTROL

In 1980, Japan had to rely on imported oil to meet 65% of its energy demand. Efforts have been made to reduce dependency on imported coal by increasing nuclear power and the import of coal and liquefied natural gas (LNG). The electric power generating capacity in 1980 was 130,000 MW, including 6,000 MW by coal. That in 1990 is expected to reach 190,000 MW, including 22,000 MW by coal.

---

*Note: There are approximately 250 yen/$; the reader is cautioned that translation of cost estimates from yen to dollars will not necessarily relate costs in Japan to costs in the United States since many cost components are not equivalent in the two countries.

Figures 1 and 2 show the ambient SO_2 and NO_2, respectively, concentrations and capacities of FGD and NO_x removal plants. The SO_2 concentrations have continued to decrease since 1968, while NO_2 concentrations reached a maximum in 1980 and have since decreased. Both the SO_2 and NO_2 concentrations in nearly all regions meet the stringent ambient air quality standards -- 0.04 ppm in daily average (equivalent to 0.016 ppm in yearly average) for SO_2 and 0.04-0.06 ppm in daily average (equivalent to 0.02-0.03 ppm in yearly average) for NO_2.

In 1984 the total number of FGD plants in Japan reached 1,400, with a total capacity of treating 130,000 Nm^3/h of flue gas (43,000 MW equivalent). About 120 plants (47% of total capacity) use the wet lime/limestone process to by-produce salable gypsum, 70 plants (15% of total capacity) use the indirect or modified lime/limestone process to by-produce salable gypsum, and 30 plants (8% of total capacity) by-produce sulfuric acid, ammonium sulfate, and elemental sulfur. Nearly all of the rest use sodium scrubbing to by-produce sodium sulfite for paper mills, sodium sulfate for the glass industry, or waste sodium sulfate/sulfite liquor. About 170 plants for selective catalytic reduction (SCR) of NO_x have been operated with a total capacity of treating 93,000,000 Nm^3/h of flue gas (31,000 MW equivalent).

About 40 coal-fired utility boilers are in operation. Most of the boilers use FGD to remove 85-98% of SO_2 to give 30-100 ppm SO_2 with 20-100 mg/Nm^3 of dust. Twenty boilers use SCR in addition to FGD to reduce NO_x concentrations to 50-150 ppm, removing 55-85% of NO_x. Coal-fired boilers without SCR reduce NO_x to 150-300 ppm by combustion modification (CM), including a low-NO_x burner. Figure 3 shows an example of the combination of CM, SCR, and FGD for a coal-fired boiler.

FGD FOR COAL-FIRED BOILERS

Table 1 lists major coal-fired boilers and their FGD and SCR plants. All of the coal-fired boilers have ESPs to reduce particulates to 50-800 mg/Nm^3 -- a removal efficiency of 96-99.8%. All of the FGD plants use the wet lime/limestone process, which can be divided into six types as shown in Figure 4 and Table 2. Type I produces a disposable sludge consisting mainly of calcium sulfite. This type of FGD system is simple and is popular in the U.S. but has been applied to only one plant in Japan because of the lack of space for sludge disposal.

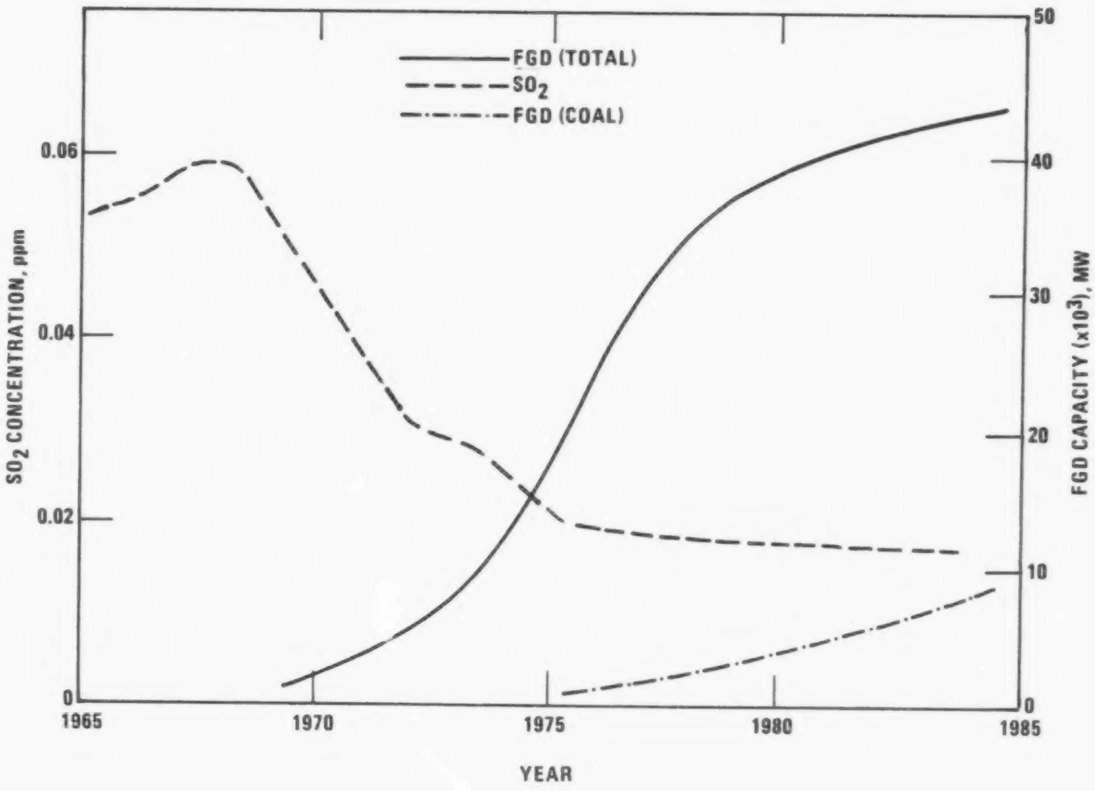


Figure 1. Annual average ambient SO_2 concentrations in 15 major cities and industrial regions and capacity of FGD plants.

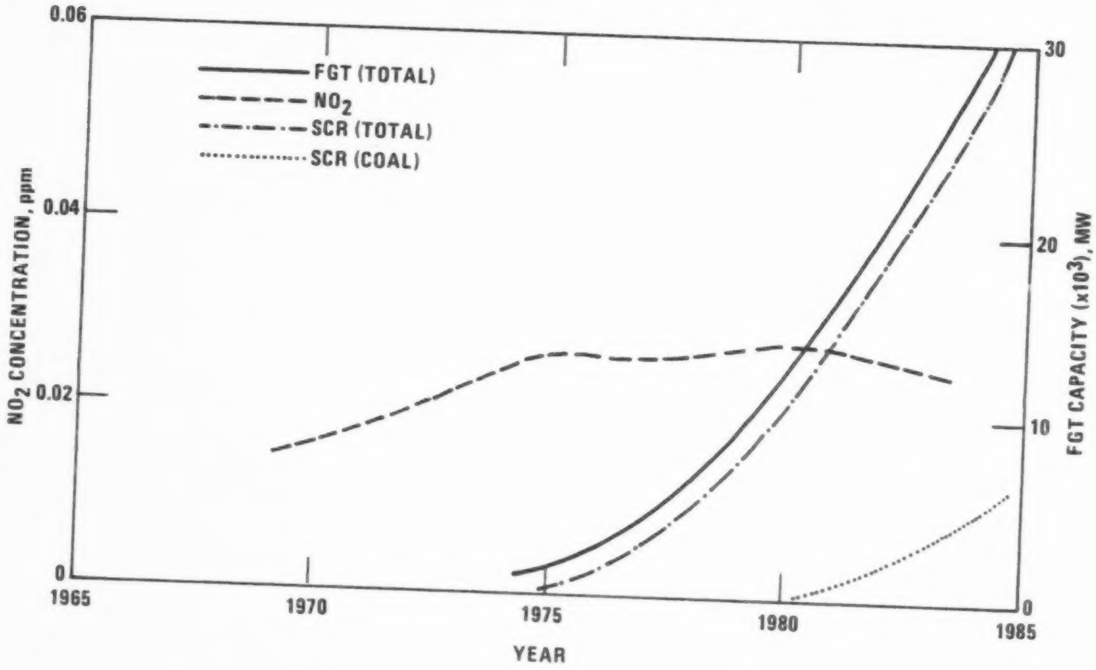
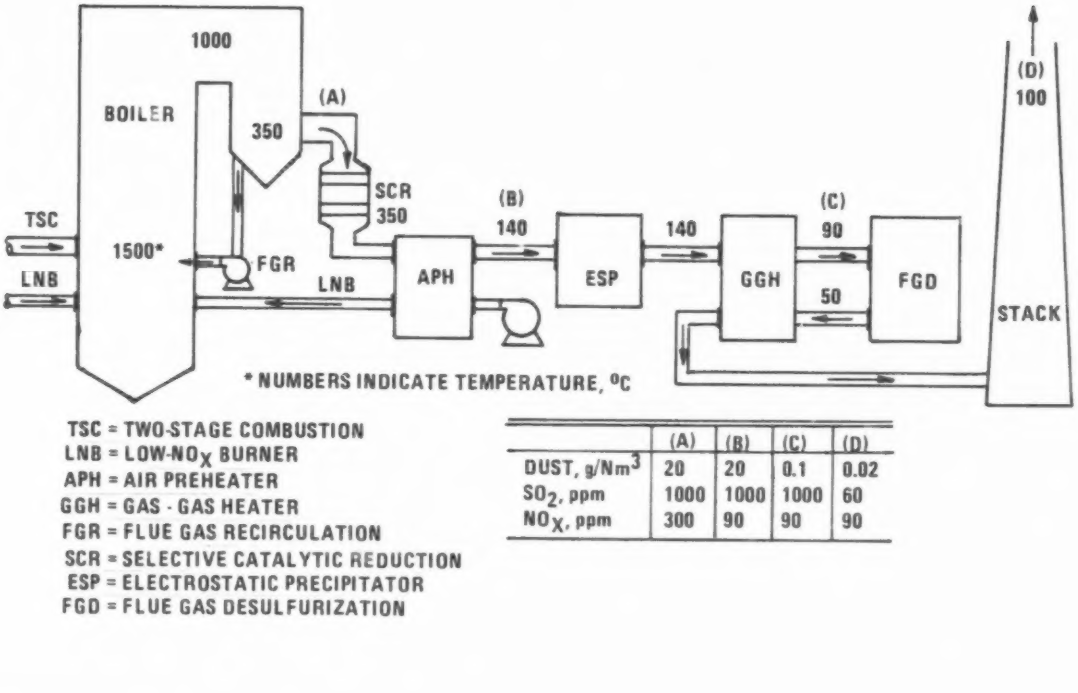


Figure 2. Annual average ambient NO_2 concentrations in 15 major cities and industrial regions and capacity of flue gas treatment (FGT) plants for NO_x removal.


1000
BOILER
350
(A)
SCR
350
TSC
1500*
FGR
LNB
LNB
APH
(B)
140
ESP
140
GGH
(C)
90
50
FGD
(D)
100
STACK
* NUMBERS INDICATE TEMPERATURE, °C

TSC = TWO-STAGE COMBUSTION
LNB = LOW-NO_X BURNER
APH = AIR PREHEATER
GGH = GAS - GAS HEATER
FGR = FLUE GAS RECIRCULATION
SCR = SELECTIVE CATALYTIC REDUCTION
ESP = ELECTROSTATIC PRECIPITATOR
FGD = FLUE GAS DESULFURIZATION

	(A)	(B)	(C)	(D)
DUST, g/Nm^3	20	20	0.1	0.02
SO_2, ppm	1000	1000	1000	60
NO_X, ppm	300	90	90	90

Figure 3. Typical flue gas treatment system for a coal-fired boiler.

TABLE 1. FGD AND SCR UNITS FOR COAL-FIRED BOILERS

Owner	Plant Site	Boiler (MW)	FGD Constructor	FGD Completed	FGD Type	SCR Constructor	SCR Completed	SCR Type
Mitsui Aluminum	Omuta	156	MMMC[a]	1972	I	-	-	-
Mitsui Aluminum	Omuta	175	MMMC	1975	II	-	-	-
EPDC	Takasago	250x2	MMMC	1975, 76	II	-	-	-
EPDC	Isogo	265x2	IHI[b]	1976	III	-	-	-
EPDC	Takehara	250	BHK[c]	1977	III	BHK, KHI[d]	1980	L[e]
EPDC	Takehara	700	IHI	1983	III	BHK	1983	L
EPDC	Matsushima	500x2[f]	IHI, BHK	1981	IV	-	-	-
EPDC	Ishikawa	156x2	IHI	1986	III	-	-	-
Chugoku Elec.	Shimonoseki	175	MHI[g]	1979	IV	MHI	1980	H[h]
Chugoku Elec.	Shin-Ube	75x2	MHI	1982	IV	MHI	1982	H
Chugoku Elec.	Shin-Ube	156	MHI	1982	IV	MHI	1982	H
Chugoku Elec.	Mizushima	125 & 156	BHK	1984	IV	BHK	1984	H
Chugoku Elec.	Shin-Onoda	500	IHI	1986	IV	IHI	1985	H
Chugoku Elec.	Shin-Onoda	500	IHI	1987	IV	IHI	1987	H
Hokkaido Elec.	Tomato	350[i]	BHK	1980	IV	BHK	1980	L
Hokkaido Elec.	Tomato	600	MHI	1984	IV	-	-	-
Joban Joint	Nakoso[j]	600	MHI	1983	IV	MHI	1983	H
Joban Joint	Nakoso[j]	600	MHI	1983	IV	IHI	1983	H
Kyushu Elec.	Omura	156	MHI	1982	IV	-	-	-
Kyushu Elec.	Minato	156	MMMC	1983	III	MHI	1983	H
Kyushu Elec.	Matsuura	700	-	1987	-	MHI	1987	H
Sakata Joint	Sakata	350	MHI	1984	IV	MHI	1984	H
Sakata Joint	Sakata	350	MHI	1987	IV	MHI	1987	H
Shikoku Elec.	Saijo	156	KHI	1983	VI	MHI	1983	H
Shikoku Elec.	Saijo	250	KHI	1984	VI	IHI	1984	H
Toboku Elec.	Sendai	175x2	BHK	1983	VI	BHK	1983	H
Tokyo Elec.	Yokosuka[k]	265	MHI	1985	IV	MHI	1984	H
Tokyo Elec.	Yokosuka[k]	265	BHK	1985	IV	BHK	1985	H
Toyama Joint	Toyama	200x2	Chiyoda	1984	V	BHK	1984	H

[a] Mitsui Miike Machinery Co.

[b] Ishikawajima-Harima Heavy Industries.

[c] Babcock Hitachi K.K.

[d] Kawasaki Heavy Industries.

[e] Low-dust system.

[f] Subjecting 75% of gas to FGD.

[g] Mitsubishi Heavy Industries.

[h] High-dust system.

[i] Subjecting 50% of gas to FGD and 25% of gas to SCR.

[j] Burns both oil and coal.

[k] Burns a coal/oil mixture.

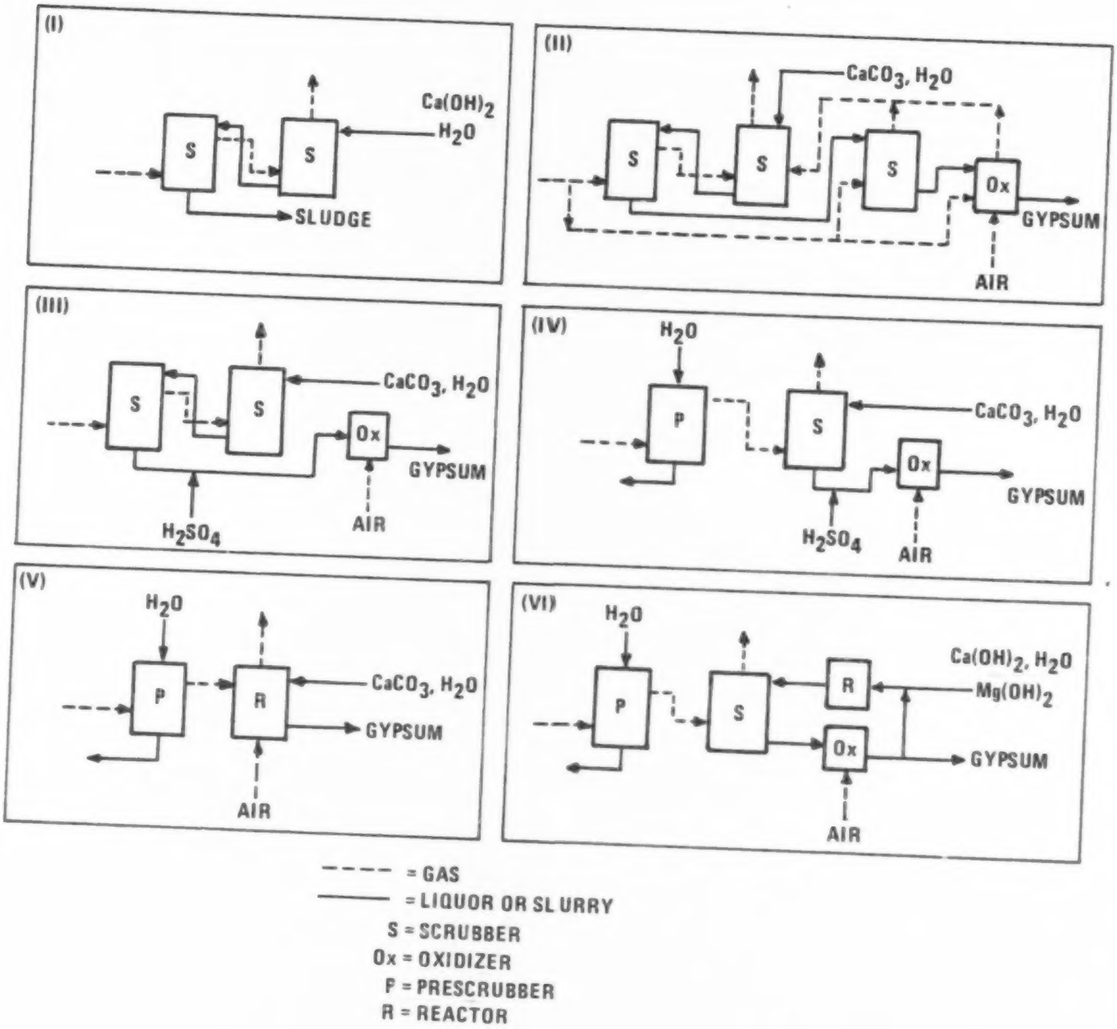

(I)
S
S
Ca(OH)$_2$
H$_2$O
SLUDGE
(II)
CaCO$_3$, H$_2$O
S
S
S
Ox
GYPSUM
AIR
(III)
S
S
CaCO$_3$, H$_2$O
Ox
GYPSUM
H$_2$SO$_4$
AIR
(IV)
H$_2$O
P
S
CaCO$_3$, H$_2$O
Ox
GYPSUM
H$_2$SO$_4$
AIR
(V)
H$_2$O
P
R
CaCO$_3$, H$_2$O
GYPSUM
AIR
(VI)
H$_2$O
P
S
R
Ca(OH)$_2$, H$_2$O
Mg(OH)$_2$
Ox
GYPSUM
AIR
= GAS
= LIQUOR OR SLURRY
S = SCRUBBER
Ox = OXIDIZER
P = PRESCRUBBER
R = REACTOR

Figure 4. Types of wet lime/limestone processes.

TABLE 2. CLASSIFICATION OF WET LIME/LIMESTONE PROCESSES

Type	By-Product	Absorbent	Additive	Prescrubber[a]	Sulfuric Acid
I	Sludge	$Ca(OH)_2$	None	None	None
II	Gypsum	$CaCO_3$	Sodium	None	None
III	Gypsum	$CaCO_3$	Sodium	None	Yes
IV	Gypsum	$CaCO_3$	None	Yes	Yes
V	Gypsum	$CaCO_3$	None	Yes	None
VI	Gypsum	$Ca(OH)_2$	$Mg(OH)_2$[b]	Yes	None

[a] With a separate liquor loop.
[b] No need when lime contains over 1% MgO.

Other types of FGD processes by-produce gypsum by oxidation of calcium sulfite with air. Since Japan has no natural gypsum resources, gypsum is a suitable by-product of FGD particularly for coal-fired boilers, because a small amount of fly ash in the by-product gypsum does not prevent its use for wallboard or as an additive to cement. To obtain salable gypsum, complete oxidation is desired, which is attained by lowering the pH of the calcium sulfite slurry from 5.5-6 to 4-4.5 prior to the oxidation step. The Type II FGD system uses an extra scrubber to lower the pH by further SO_2 absorption and adds sodium hydroxide or sulfate to promote SO_2 absorption and sulfite oxidation. The Type II system is used at three FGD plants.

In Type III plants the pH of the slurry is lowered by adding a small amount of sulfuric acid. Type III plants require lower investment costs than Type II plants, and may be preferable where sulfuric acid is available for a reasonable price. The Type III system originally had two scrubbers in series and often uses a sodium compound to promote the reactions. Recently Mitsui Engineering Co. (formerly Mitsui Miike Machinery Co., MMMC) completed two new plants with a single scrubber -- one for Kyushu Electric at Minato and the other for Mitsui Coal Mining at Omuta (47 MW).

Type IV FGD plants use a prescrubber with a separate liquor loop and use sulfuric acid for pH adjustment. This sytem was developed by Mitsubishi Heavy Industries (MHI) and has been applied to many new coal-fired boilers. The prescrubber in the system has the following functions: (1) it removes fly ash in order to increase the purity of by-product gypsum, (2) it removes chloride in the flue gas -- chloride tends to increase corrosion and to lower SO_2 removal efficiency, (3) it cools the gas to prevent scaling and to protect scrubber linings, and (4) it removes fluoride in the flue gas which tends to lower SO_2 removal efficiency in combination with aluminum derived from coal ash.

It appears that fluoride and aluminum combine to form complex ions which prevent the chemical reactions (1). The combined effect of fluoride and aluminum is especially noticeable with certain types of coals or a blend of coals (2). A prescrubber may not be needed for a coal containing little fluoride or when a reaction promoter, such as sodium, magnesium, or organic acid, is added. Without the prescrubber, a small amount of fly ash goes into the by-product gypsum but does not affect its suitability for use in cement or wallboard. Somewhat offsetting its beneficial effects, the prescrubber raises the FGD plant cost by 3-7% and increases the amount of wastewater produced.

Recently two new FGD processes have been applied to coal-fired boilers: the Chiyoda Jet Bubbling Reactor Process (Type V) and the Kawasaki magnesium/gypsum process (Type IV). Both processes attain perfect oxidation without using sulfuric acid and produce salable gypsum. The operational parameters of new FGD plants for coal-fired boilers are shown in Table 3. All of the plants have been operated without trouble since their start-up.

All of the new FGD plants planned for new coal-fired boilers will also use the gypsum by-producing FGD process because the gypsum in Japan will continue to be in short supply at least for several years. Spray dryer type dry lime scrubbing processes may not be used in Japan where over 95% SO_2 removal efficiency is wanted, and there is little landspace for by-product disposal.

RECENT IMPROVEMENTS IN FGD FOR COAL-FIRED BOILERS

Cost Reduction

Since technology has already been developed to prevent scaling, a major problem in the wet lime/limestone FGD process, recent efforts have been focused on making the process more cost effective through reduction of investment cost and power consumption. The investment cost for the wet lime/limestone process for a coal-fired boiler was about 19,000 yen/kW in 1975, and increased to about 35,000 yen/kW in 1979 mainly by inflation. However, most of the FGD plants constructed in 1983 and 1984 cost between 19,000 and 24,000 yen/kW (Table 3). These reduced costs may be due to: (1) technology improvements which allow a plant to be simplified without reducing its reliability and SO_2 removal efficiency, (2) construction of many FGD plants which allows plant constructors to realize their return on R&D expenses, and (3) demand for less costly plants, particularly because of the recent economic downturn.

The power consumption of FGD plants constructed in 1975-1978 for coal-fired boilers reaches 2.4-2.6% of power generated by the boiler. The consumption of FGD plants completed in 1983-1984 reached 1.7-2.1% (Table 3). The reduction is achieved by the use of a scrubber with a low pressure drop, such as spray tower or plastic-grid-packed tower. Chiyoda's JBR process plants consume less power because they have no slurry recirculation pumps.

TABLE 3. FGD PLANTS FOR COAL-FIRED BOILERS (1983-84)

Owner/ Station	Joban/ Nakoso[a]	EPDC/ Takehara	Kyushu/ Minato	Shikoku/ Saijo	Toyama/ Toyama
Boiler capacity, MW	600x2	700	156	156	200x2
Boiler start-up year	1983	1983	1983	1983	1984
FGD type	IV	III	III	VI	V
FGD constructor	MHI	IHI	MMMC	KHI	Chiyoda
Gas treated, 1,000 Nm^3/h	1,860x2	2,200	560	560	730x2
Inlet SO_2, ppm	1,000	700	1,520	700-800	630
Inlet dust, mg/Nm^3	150	30-150	10	30-100	100
1st scrubber (prescrubber)	spray	spray	none	spray	venturi
o pH	1	4.5-5	-	1	1
o L/G, liter/Nm^3	2	5	-	2	1
2nd scrubber (scrubber)	packed	spray	spray	spray	JBR[b]
o pH	5.5	5.5-6	5.5	5.5-6	4
o L/G, liter/Nm^3	20	15	16	4	-
o Outlet SO_2, ppm	40	30-35	10-30	15-20	63
o Outlet dust, mg/Nm^3	45	10-20	10-20	10-20	10-20
SO_2 removal, %[c]	96	95	98-99	98	90
Dust removal, %[c]	70	70-80	80-90	70-80	80-90
Gas reheating	GGS & SGH[d]	GGH	GGH	GGH	GGH
Pressure drop, mm H_2O[e]	340	350	280	480	630
Wastewater, m^3/h	13	25	5	5	4
Power consumption, %[f]	1.8	2.1	2.0	1.9	1.7
Investment cost, yen/kW[g]	21,000	20,000	24,000	20,000	19,000

[a] Burning oil and coal (90:10).

[b] Jet bubbling reactor.

[c] Slightly lower after GGH.

[d] Steam-gas heater (to 120°C).

[e] By scrubbers, mist eliminators, and GGH.

[f] Percent of power generated by the boiler.

[g] Including gas reheating system and civil engineering.

Computer control, as shown in Figure 5, also reduces the power consumption by responding quickly to changes in inlet conditions. Due to automatic control, new FGD plants for coal-fired boilers are usually operated by two persons per shift, instead of four or five persons for old plants. The FGD plants are normally operated for 11 months continuously and then shut down for about 1 month for annual boiler maintenance.

The annualized operation cost of a wet limestone/gypsum process FGD plant for a coal-fired boiler may be about 1.4 yen/kW including 7 years depreciation and 10% interest, assuming an investment cost of 20,000 yen/kW and power consumption of 1.8%.

New System

The new FGD plants at the Yokosuka Station of Tokyo Electric for 265 MW COM-fired boilers (50% coal and 50% oil, Table 1) use non-leak type gas reheaters (Figure 6). The No. 1 unit constructed by MHI uses a multi-tube system through which hot water is circulated by a pump. The No. 2 unit constructed by BHK uses a heat-pipe system by which heat is transferred by evaporation and condensation of water. The FGD plants are designed to reduce SO_2 from 790 to 76 ppm and dust from 150 to 20 mg/Nm^3 and have been operated without trouble since the start-up in early 1985. The reheaters are much bigger than Ljumgstrom type gas reheaters and may cost a little more. A small amount of dust tends to deposit in the reheaters but can be removed by soot blowing.

Particulate Removal

In Japan, baghouses are not yet used for large amounts of gas, such as produced by coal-fired utility boilers, because of their high pressure drop and the possibility of malfunction. Cold-side ESPs generally are used with coal-fired boilers except for three hot-side ESPs constructed between 1979 and 1982. Although ESPs for coal-fired boilers remove 96-99.8% of particulates, an FGD system also is used for the additional particulate removal required. Between 0.1 and 1 g/Nm^3 of the dust at the ESP outlet is reduced to 0.02-0.1 g/Nm^3 by the FGD system. In order to obtain a higher dust removal efficiency from a scrubber system, a larger L/G ratio must be used which, in turn, causes a higher pressure drop. To increase the dust removal efficiency of an ESP, a larger ESP and higher power consumption are required, although the removal efficiency also depends on the composition of the fly ash.

Figure 7 shows dust removal costs for reducing particulates to 0.05 g/Nm^3 using the combination of an ESP and a scrubber system. With a decrease in ESP efficiency, the investment depreciation costs decrease, but the scrubber system must be operated with a high dust removal efficiency, thereby consuming a large amount of power. The total cost may be lowest when the ESP outlet particulate concentration is about 0.2 g/Nm^3.

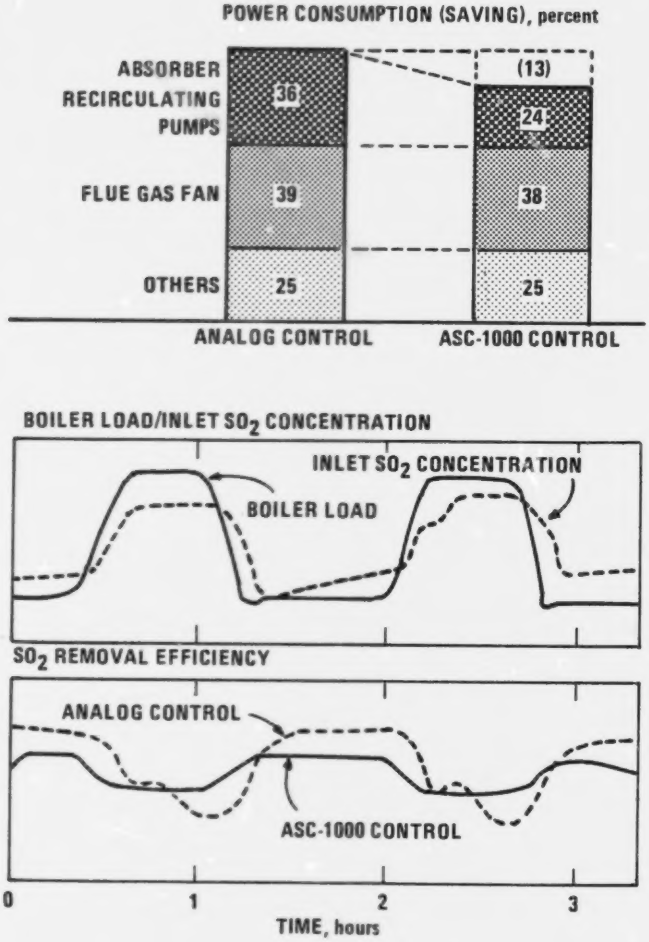


Figure 5. Example of MHI's ASC-1000 control of an FGD system and resultant power saving.

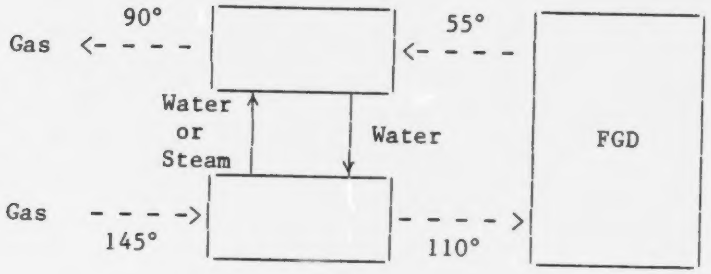

90°
Gas
55°
Water
or
Steam
Water
FGD
Gas
145°
110°

Figure 6. Non-leak type gas reheating system (Yokosuka plant, Tokyo Electric)

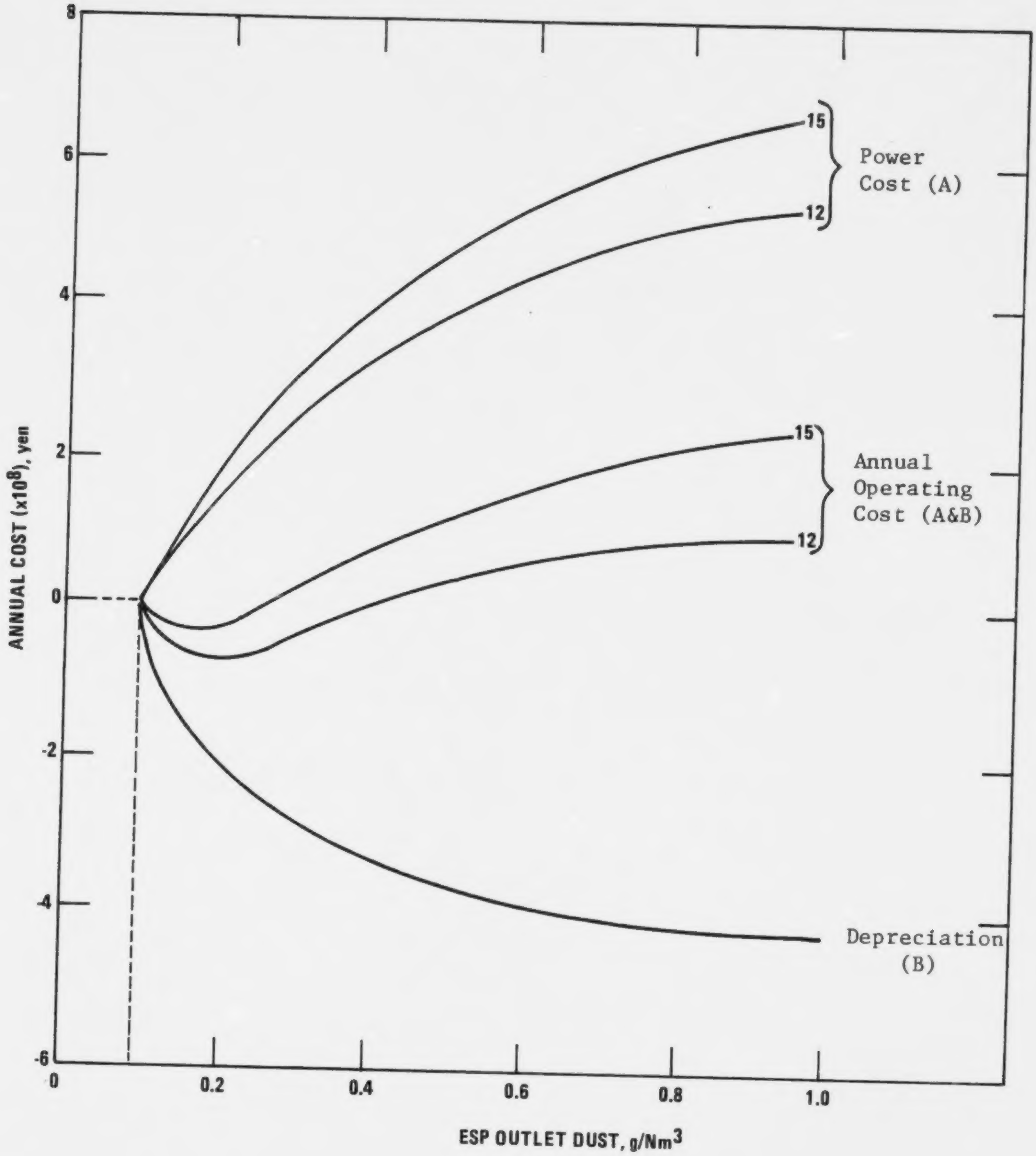


Figure 7. Cost comparison of dust removal by ESP and FGD (1000 MW) coal-fired boiler. Outlet dust 50 mg/Nm^3 (3).

Note: The figure shows cost comparison taking the ESP outlet dust 0.1_g as the basis (zero), for two cases with the power price of 15 and 12 yen/kWh.

Figure 8 shows the particle size distribution of fly ash from pulverized coal combustion at three stages of dust removal. The dust concentration at the GGH inlet is 227 mg/Nm^3, with particles ranging in size from 0.2 to 3 μm. These sizes indicate that particulates larger than 3 μm are caught by the ESP. In the scrubber and in the mist eliminator within the scrubber, the dust is reduced to 61.7 mg/Nm^3 and most of the particles between 1.5 and 3 μm are removed. With an efficient mist eliminator between the scrubber and the GGH, particulates are further reduced to 11.9 mg/Nm^3, with most of the remaining particles ranging from 0.2 to 1 μm.

McElroy found that particles about 0.2 μm in size are relatively rich in heavy metals such as arsenic and zinc (5). Those elements and their compounds are vaporized at high combustion temperatures and condense on cooling to form very fine particles. The behavior of these fine particles merits further study, although they may not have an adverse effect on human health because they exist in such small quantities. Baghouses may be preferred to ESPs for removing the submicron particles.

Gas-Gas Heater (GGH)

All FGD plants completed between 1979 and 1984 for coal-fired boilers have a Ljungstrom type rotary gas-gas heater (GGH) as shown in Figure 3. Although GGH is costly -- about 10% of the FGD investment -- it is a more economical method of gas reheating than low-sulfur oil firing.

One of the problems associated with the GGH is dust deposition. A small portion of the dust leaving the ESP is deposited in the GGH. SO_3 in the flue gas increases the dust deposition. The SO_3 content of the gas from a coal-fired boiler leaving the ESP is usually about 3 ppm. In this case, the dust deposition is appreciable when the inlet dust concentration is 0.1-0.2 g/Nm^3, and the GGH may have to be water-washed two or three times a year. The deposition is reduced with a lower inlet dust content. On the other hand, when the inlet dust concentration is higher, the deposit tends to be soft and can be removed fairly easily by soot blowing.

For a new coal-fired boiler, a very low dust emission (20-30 mg/Nm^3) is often required by local regulation. Therefore, new FGD plants for coal-fired boilers use an efficient ESP to reduce particulates below 100 ppm, so that the dust content is reduced to 20-30 mg/Nm^3 by the FGD plant. In this way, the GGH may be operated continuously for a year without waterwash.

Another problem with the GGH is gas leakage. As shown in Figure 9, the fan usually is located at the A position, causing 2-5% of the untreated gas to leak into the treated gas, lowering both the SO_2 and dust removal efficiencies. Placing the fan at the B or C position causes the cleaned gas to leak into the untreated gas, preventing the decrease in SO_2 or

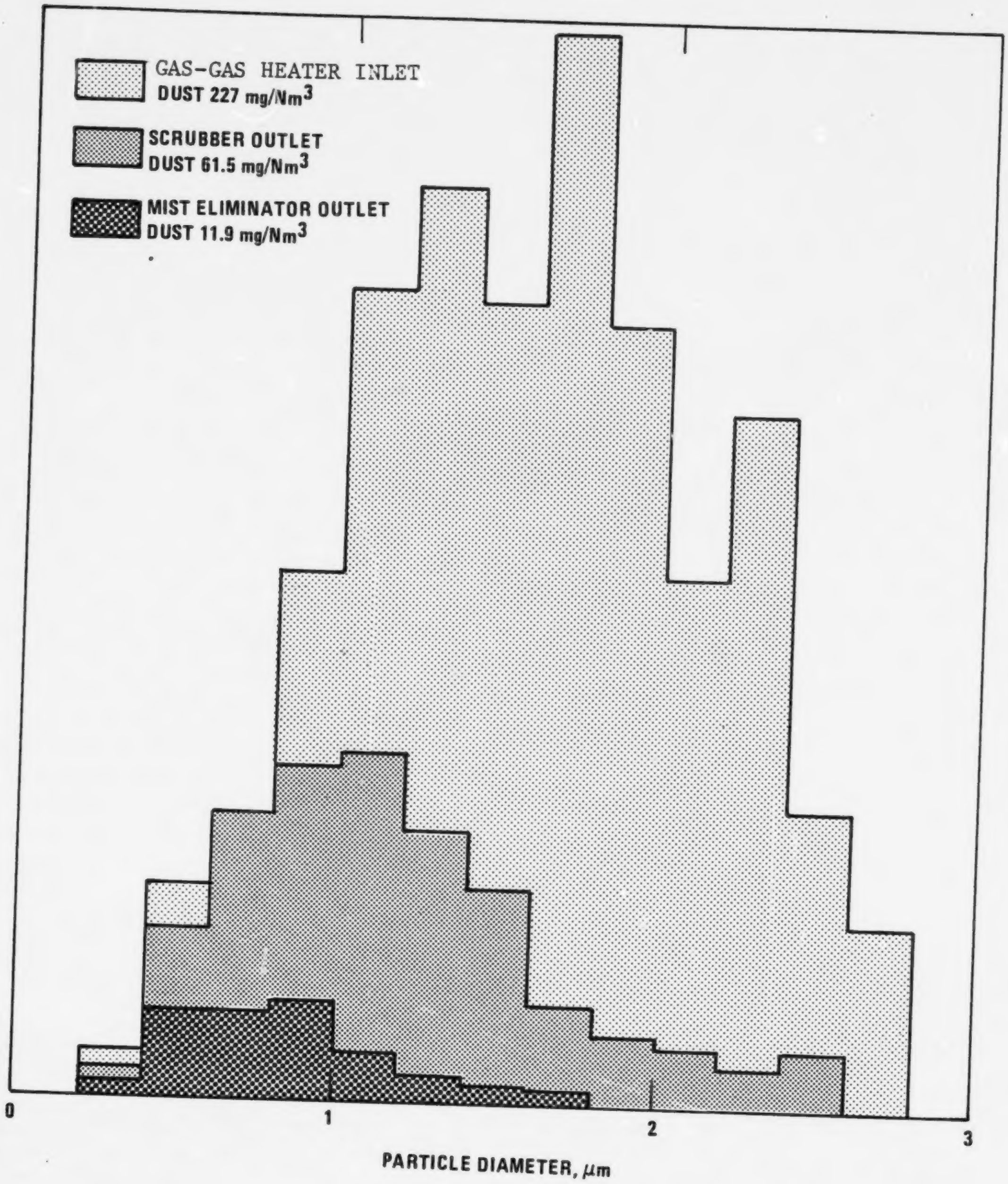


Figure 8. Particle size distribution of dust at three stages of removal (4).

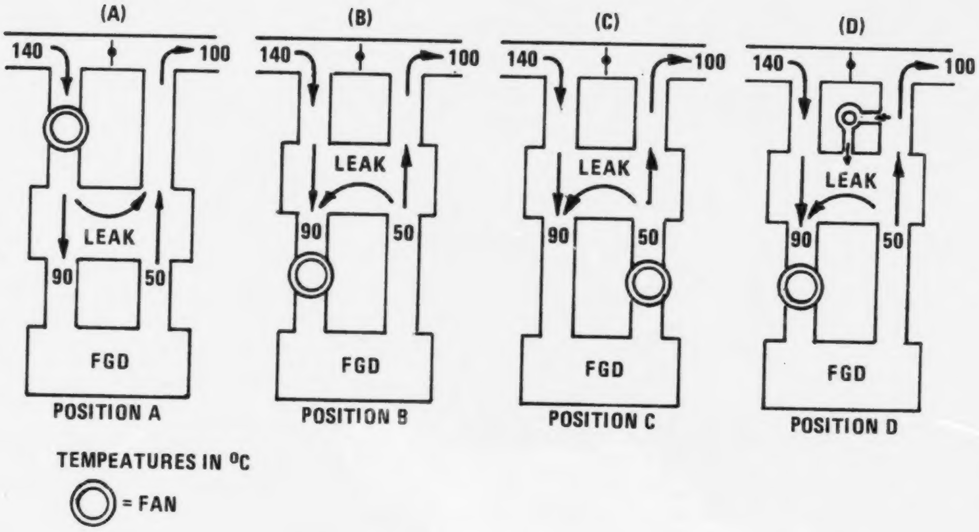

(A)
140
100
LEAK
90
50
FGD
POSITION A
(B)
140
100
LEAK
90
50
FGD
POSITION B
(C)
140
100
LEAK
90
50
FGD
POSITION C
(D)
140
100
LEAK
90
50
FGD
POSITION D
TEMPEATURES IN °C
= FAN

Figure 9. Gas leakage in rotary gas-gas heaters having fans located in four different positions.

dust removal efficiencies, but requiring corrosion resistant material because of acid condensation at the low temperature.

Various improvements have been made in the GGH. For example, the GGH at Joban Power's Nakoso station has a fan at the A position with less than 2% leakage (because of an improved mechanical seal). The GGH at Takehara No. 3 unit of EPDC has a fan at the B position and is equipped with a scavenging fan as shown in D of Figure 9: this eliminates the slight decrease of SO_2 and dust removal efficiencies caused by the untreated gas remaining between the heating elements.

NO_x AND SIMULTANEOUS SO_2/NO_x REMOVAL PROCESSES

Selective Catalytic Reduction (SCR) of NO_x

SCR that uses ammonia and a catalyst at 200-400°C has become popular in Japan due to its simplicity, reliability (enabling unattended automatic control), and lack of a by-product disposal problem. About 170 commercial plants with a total capacity of 93,000,000 Nm^3/hr (31,000 MW equivalent) are in operation, removing 55-90% of NO_x (Figure 2 and Tables 4 and 5). Nearly 90% of the total capacity is for utility boilers; the rest is for industrial boilers, iron ore sintering machines, various furnaces, etc.

SCR plants for coal- and oil-fired utility boilers use parallel flow catalysts such as honeycomb type or plate type while those for gas-fired boilers use a pellet catalyst. Most of the SCR plants for coal-fired boilers use the "high-dust" system which treats flue gas from the boiler economizer at 300-400° C with full dust load (Figure 3); three plants use the "low-dust" system by which the flue gas from the economizer is first treated by a hot-side ESP and then by SCR (Table 1).

Early in its development, SCR had serious problems, which have been solved by the improvements in technology. Catalyst poisoning by SO_x has been prevented by the use of TiO_2 as a base catalyst. Catalyst erosion by fly ash from coal has been minimized by the use of a hard catalyst and a dummy spacer. Ammonium bisulfate deposits in the air preheater have been prevented by reducing unreacted NH_3 below 3 ppm. The reduction of the unreacted NH_3 also prevents the contamination of fly ash by ammonia. The unreacted NH_3 is caught by a wet FGD unit downstream but does not affect the FGD operation. One of the problems has been the increase of SO_3 in flue gas due to the oxidation of SO_2 by the SCR catalyst -- SO_3 promotes the deposit formation in the gas reheating heater. The problem has been minimized by the use of a low-oxidation catalyst with an oxidation ratio of 0.2-0.5%.

The catalyst life is about 3 years for coal-, 7 years for oil-, and over 7 years for gas-fired flue gas. There has been little spent catalyst yet because of the long catalyst life. The investment cost is 6000-8000 yen/kW for coal, 3000-5000 yen/kW for oil, and about 2500 yen/kW for gas,

TABLE 4. SCR PLANTS IN JAPAN (Early 1985)

Gas Source	Number	Capacity (1,000 Nm^3)	Capacity (MW)
Utility boiler, Coal	20	14,500	4,800
Oil	57	57,000	19,000
Gas	6	11,300	3,900
Other sources	85	9,900	3,300
Total	168	92,700	31,000

TABLE 5. MAJOR SCR PLANTS (By end of 1983)

Plant Constructor	Utility Boiler		Other Sources	
	Number	Capacity (1,000 Nm^3/h)	Number	Capacity (1,000 Nm^3/h)
Hitachi Ltd. and Babcock Hitachi (BHK)	21	19,540	8	1,630
Hitachi Zosen			9	1,867
Ishikawajima Harima H.I. (IHI)	15	18,505	1	200
JGC Corporation			5	393
Kawasaki H.I. (KHI)	2[a]	750	1	25
Mitsubishi H.I. (MHI)	32	25,950	7	713
Mitsubishi Kakoki (MKK)			10	244
Mitsui Toatsu Chemical			13[b]	1,297
Mitsui Engineering			12	1,320
Sumitomo Chemical and Sumitomo Chemical Engineering (SCEC)	—	—	12	1,129
Total	70	64,745	78	8,818

[a] One of the plants in the U.S.

[b] Five of the plants in U.S.S.R. at a nitrophosphate factory.

including the initial charge of catalyst. The annualized operation cost, including 7 years depreciation and 10% interest, is 0.5-0.7 yen/kWh for coal, 0.2-0.3 yen/kWh for oil, and about 0.15 yen/kWh for gas. Nearly all of the new coal-fired boilers and gas-fired combined cycle power plants are to use SCR to reduce NO_x concentrations to 60-100 ppm (at 6% O_2 basis) to meet the stringent regulations in Japan. Although SCR is simple and reliable, and has become popular in Japan, it is far more costly than combustion modifications including low-NO_x burner, two-stage combustion, and flue gas recirculation, by which NO_x in coal-firing flue gas can be reduced to 150-300 ppm (6, 7).

Selective Noncatalytic Reduction (SNR or Thermal DeNO_x)

Thirty-three SNR plants have been operated in Japan as shown in Table 6. Those plants treat flue gases containing little or no SO_x (below 100 ppm) and remove 20-60% of NO_x by injecting 0.4-2 mol NH_3 to 1 mol NO_x at 800-1,000°C. SNR may be suitable for a furnace with relatively long gas retention time at 800-1,000°C or for dirty gas (e.g., gas from city refuse incinerator in which the SCR catalyst may be degradated) but may not be useful for SO_x-rich gas because SNR usually produces a considerable amount of unreacted NH_3 which may combine with SO_3 causing an ammonium bisulfate problem.

TABLE 6. SNR PLANTS IN JAPAN (Late 1984)

Process Developer, Constructor	Flue Gas Source	Number of Units	Total Capacity (1,000 Nm^3/h)	NO_x Removal (%)	Year Completed
Exxon	Industrial boiler and furnace	8	2,211	20-50	1976-84
MHI	Utility boiler	1	1,000	30-40	1976
MHI	Incinerator	5	250	50-60	1983-84
MKK	Industrial boiler and furnace	19	86	40-60	1976-78
Total		33	3,547 (1,190 MW equivalent)		

Activated Coal Process for Simultaneous Removal

Electric Power Development Co. (EPDC), jointly with Sumitomo Heavy Industries (SHI), has developed the activated carbon process to by-produce elemental sulfur. A demonstration plant with a capacity of treating 300,000 Nm^3/h of flue gas from a coal-fired boiler started operation in 1984 at EPDC's Matsushima Station. The plant is designed to remove more than 95% of SO_2 with 25% of NO_x. Concentrated SO_2 that is released by heating the coke loaded with SO_2 is treated by a coal reactor and Claus furnaces to produce elemental sulfur. However, no test results at the demonstration plant are available.

Mitsui Mining Co., jointly with Mitsui Engineering Co. (formerly Mitsui Miike Machinery Co.) and Bergbau Forschung, has also developed a similar activated coke process and has operated a pilot plant with a 30,000 Nm^3/h capacity for coal-firing flue gas. The plant has been operated successfully removing 50-85% of NO_x with over 98% of SO_2. Mitsui Mining Co. estimates that, compared with the combined wet limestone/gypsum FGD and SCR, the activated coke process requires a little higher running cost and less investment cost, so that the annualized operation cost (including depreciation) may be less.

Those processes can attain a higher sulfur recovery efficiency than Foster Wheeler's $ReSO_x$ process (90% vs. 60% for $ReSO_x$) but are more complex, requiring Claus furnaces. The activated coke process might be applied to oil refineries where there are existing Claus furnaces, but seems too complex to be used at power plants. High coke consumption may present another problem. Mitsui Mining is operating an activated coke production pilot plant in search for the production of less costly activated coke.

Other Simultaneous Removal Processes

The Electron beam process, originally developed by Ebara Corp. in Japan, is now being tested in the U.S. and West Germany. The process can remove over 90% of SO_2 with 80% of NO_x and is advantageous in: (1) being a dry process giving no wastewater and requiring no gas reheating, (2) simpleness, and (3) converting SO_2 and NO_x to ammonium sulfate and nitrate useful for fertilizers. On the other hand, the process consumes much electric power -- about 3%, compared with about 2% by wet FGD and 0.2% by SCR. The process may not be commercialized in Japan where there is very little demand for ammonium nitrate fertilizer.

The Yokkaichi plant, using the Shell copper oxide process for an oil-fired industrial boiler, has been shut down. There have been few new developments with other dry simultaneous removal processes.

A wet magnesium scrubbing plant by the Fujikasui process using ClO_2 as the oxidizing agent was put into operation in 1984 to remove about 40% of NO_x with over 90% of SO_2 in a flue gas from an industrial oil-fired boiler (67 MW equivalent). Wastewater containing magnesium sulfate, nitrate, nitrite, and chloride is treated, together with a much larger amount of wastewater produced in the factory. There have been no new developments in other wet processes.

Wet simultaneous removal processes may not be suitable for a large gas source because the processes have either one or two of the following disadvantages: (1) a costly oxidizing agent is needed, (2) wastewater containing nitrogen compounds must be treated, and (3) the process is complex.

Fluidized-Bed Combustion (FBC) of Coal

EPDC tested FBC with a 6 MW equivalent pilot plant (8) and is to start construction of a larger test plant (50 MW equivalent) in 1985. Two commercial plants for industrial use -- a 17 MW equivalent plant of Sakito Salt and a 35 MW equivalent plant of Mitsui Aluminum -- started operation in 1984. The former was constructed by MHI working with FCC in the U.S., while the latter was constructed by KHI based on test results from EPDC's pilot plant. Both have a main bed cell and a carbon burnup cell, use coal under 15 mm in size, and achieve 98% combustion efficiency. The former uses a blend of coal containing 0.9% N and 1.1% S and maintains NO_x at 200-250 ppm while removing about 70% of SO_2 using limestone (under 3 mm) at 4 mol CaO to 1 mol SO_2 (9). The by-products have been thrown away so far. The latter uses a blend of coal containing 1.1% N and 1.4% S and maintains NO_x of around 85 ppm (at 4% O_2) by two-stage combustion and SO_2 at 100-110 ppm by using limestone (1-3 mm) at 4.5 mol CaO to 1 mol SO_2. The by-product ash (rich in lime) is used to treat red mud, the by-product of aluminum production from bauxite (10).

FBC, however, may not be suitable for utility boilers in Japan because the process: (1) is not conveniently applied when there are frequent boiler load changes or start-up and shutdown cycles; (2) is subject to considerable heat loss during shutdown because of the large heat content of the bed material; (3) is not easily used to meet stringent SO_x and NO_x regulations; and (4) creates a disposal problem because of the large amount of lime-rich ash by-product.

ESTIMATED COSTS FOR POLLUTION CONTROL AND EVALUATION OF CONTROL METHODS

Power Generation and Pollution Control Costs

Costs of power generation by coal- and oil-fired boilers, including pollution control, are calculated based on the assumptions shown in Table 7. The calculated costs are shown in Table 8. The investment cost for coal-firing is much higher than for oil-firing but the annualized cost of the former is lower, even though about 20% of the total cost goes for pollution control.

TABLE 7. COAL- AND OIL-FIRED BOILER POWER GENERATION, ASSUMPTIONS FOR COST ESTIMATION: NEW UTILITY BOILERS (Two units each of 1,000 MW. SO_2 emissions = 100 ppm, NO_x emissions = 100 ppm, particulate emissions below 30 mg/Nm^3.)

	Sulfur (%)	Cost	Gas Cleaning Method
Coal	1.2	14,000 yen/ton	SCR, ESP, and FGD, as shown in Figure 3
Oil	0.2	55,000 yen/kl	Combustion modification and ESP

TABLE 8. COST OF POWER GENERATION AND POLLUTION CONTROL (1984)

	Investment Cost (yen/kW)		Annualized Cost (yen/kWh)[a]	
	Coal	Oil	Coal	Oil
Power generation	210,000	170,000	12.2[b]	17.4[c]
FGD	20,000	-	1.4	-
SCR	6,000	-	0.5	-
ESP	4,000	3,000	0.1	0.005
Other pollution control[d]	20,000	7,000	1.0	0.15
Total	260,000	180,000	15.2	17.6

[a] Including 7 years' depreciation for pollution control facilities.
[b] Including 6.4 for fuel.
[c] Including 12.9 for fuel.
[d] Ash disposal, water and noise control, etc.

The cost of oil-firing was higher in late 1972, when low-sulfur oil cost more than 60,000 yen/kl while coal cost more than 15,000 yen/ton. The estimated power generation cost at that time was about 21 yen/kWh with oil and 18 yen/kWh with coal. However, the price of oil decreased in 1983 so that the power generation cost was about equal for oil and coal, causing a delay in the construction schedule for some new coal-fired boilers. More recently, the price of coal and pollution control costs decreased so that once again coal has become more economical than oil, as shown in Table 7. The use of high-sulfur oil together with FGD and partial SCR may be of about equal or slightly greater cost than the use of low-sulfur oil.

Current power generation costs in yen/kWh for efficient existing power stations may be about 14 for coal, 17 for oil or natural gas (LNG), and 12.5 for nuclear power. It appears possible that nuclear energy costs will increase because of the requirement for further safety measures. If so, coal will be the least expensive energy source for power generation, even in Japan which has to import coal and requires stricter pollution control measures than other countries.

Acid Removal Costs

SO_2 and NO_x removal are important for prevention of acid precipitation. Table 9 compares acid removal costs by wet FGD, combustion modification (CM), and SCR. For the removal of acid (H^+), CM is the most economical, while SCR is more costly than FGD.

TABLE 9. ACID REMOVAL COSTS (Coal-Fired Boilers)

Pollutant	SO_2		NO_x						
Control technology	FGD		CM		SCR			CM(1) SCR(2)	CM(2) SCR(3)
			(1)	(2)	(1)	(2)	(3)		
Concentration, ppm									
Not treated	1500	600	600	600	600	400	250	600	600
Treated	100	50	400	250	100	100	100	100	100
Removal, %	93	92	33	58	83	75	60	83	83
Removal cost									
Yen/kWh	1.5	1.4	0.03[a]	0.1[a]	0.7	0.5	0.4	0.53	0.50
Yen/mole	7	17	1	2	9	14	18	6.6	6.3
Yen/mole H^+	3.5	8.5	1	2	9	14	18	6.6	6.3

[a] Rough figure which includes the loss of fuel from increases in the level of unburned carbon.

Discussion

Japanese FGD and SCR processes have become highly reliable and yet less costly than before. Further substantial cost reduction may be difficult with the limestone/gypsum process but may be expected with SCR, particularly after the process developers and the catalyst producers get the return for their R&D expenses. Yet SCR must be a much more costly way of NO_x abatement than combustion modification (CM). By CM, including low-NO_x burners, 50-70% of NO_x can be reduced to lower the NO_x concentrations in flue gases to 150-300 ppm for coal-, 80-130 ppm for oil-, and 40-60 ppm for gas-fired boilers. For further NO_x abatement, in-furnace NO_x reduction (IFR, or three-stage combustion, or reburning) being developed in Japan and the U.S. may be useful. Flue gas treatment methods such as SCR and SNR should be used when further NO_x abatement is needed.

Simultaneous SO_2 and NO_x removal processes seem to require substantial improvements to be applied commercially on a large scale. For the activated coke process, low-cost activated coke and the simplification of the process may be desired. For the electron beam process, cost-down of the electron beam gun and the reduction of power consumption may be desired along with the market for the by-product.

SO_2 and NO_x abatement may become more and more important also in developing countries -- the acid rain problem has spread in those countries (including Mainland China) as coal consumption increases. Further development of cost effective processes (such as a simple way of CM and limestone injection into the furnace) could be valuable for future application in those countries.

Acknowledgement

This work was sponsored by the Air and Energy Engineering Research Laboratory of the U.S. Environmental Protection Agency under contract number 68-02-3949. The EPA Project Officer is J. David Mobley in Research Triangle Park, NC.

LITERATURE CITED

1. Ando, J. and M. Mori. Hydration and Filterability of Gypsum in the Manufacture of Wet Process Phosphoric Acid. Kogyo Kagaku Zasshi, 68:2337, 1965 (in Japanese).

2. Ando, J. SO_2 Abatement for Coal-Fired Boilers in Japan. EPA-600/7-83-028 (NTIS No. PB83-225938), U.S. Environmental Protection Agency, Research Triangle Park, NC, May 1983.

3. Segawa, K., et al. Flue Gas Treatment System for Coal-Fired Boilers. Ishikawajima-Harima Engineering Review, 20(6), 1980 (in Japanese).

4. Sugita, T., H. Oguri, and Y. Sakamoto. Status of IHI Pollution Control FGD Technology. Ishikawakima-Harima Engineering Review, 21(3), 1981 (in Japanese).

5. McElroy, M.W., et al. Size Distribution of Fine Particles from Coal Combustion, Science, 215, January 1982.

6. Ando, J. NO_x Abatement for Stationary Sources in Japan. EPA-600/7-83-027 (NTIS No. PB83-207639), U.S. Environmental Protection Agency, Research Triangle Park, NC, May 1983.

7. Ando, J., and J.D. Mobley. Low-NO_x Burners for Pulverized-Coal-Fired Boilers in Japan. Presented to the Flue Gas Desulfurization Pilot Study Group of the NATO Committee on the Challenges of Modern Society, York, England, EPA-600/D-84-153 (NTIS No. PB84-201706), May 1984.

8. Koga, M., T. Shimizu, K. Ogiyama, and K. Sakamoto. 20t/h Fluidized Bed Boiler Pilot Plant. In Proceedings of the Sixth Coal Utilization Technology Symposium, Coal Mining Research Center, August 1984 (in Japanese).

9. Ichimura, S. 58.8t/h Fluidized Bed Boiler for Sakito Salt Co. Ltd. Salt Works. In: Proceedings of the Sixth Coal Utilization Technology Symposium, Coal Mining Research Center, August 1984 (in Japanese).

10. Kikuzawa, K. 120 t/h Fluidized Bed Boiler for Mitsui Aluminum Co. Ltd. Wakamatsu Works. In: Proceedings of the Sixth Coal Utilization Technology Symposium, Coal Mining Research Center, August 1984 (in Japanese).

EPA'S STATIONARY SOURCE CONTROL TECHNOLOGY RESEARCH PROGRAM

by: Carl R. Gerber
Director
Office of Environmental Engineering and Technology
Office of Research and Development
U.S. Environmental Protection Agency
Washington, DC

I would like to add my words of welcome to those voiced earlier by Julian Jones of the Air and Energy Engineering Research Laboratory, one of three engineering laboratories in EPA's Office of Research and Development. This symposium, the third in a series on SO_2 control cosponsored by the EPA and the Electric Power Research Institute (EPRI) is a major link in the cooperation between the Federal government (which regulates the emissions of air pollutants) and the private sector (which must meet these regulations and produce the equipment with which to do so). Only with cooperation and coordination of this type--at all levels-will it be possible to provide the technology that the nation, indeed the world, needs to control emissions from stationary sources at an affordable price.

While the exchange and dissemination of information is, or should be, a basic aspect of all scientific and technical endeavors, it is essential for those of us involved in government funded research. First, there is the fact that such work is funded with public dollars and the results are a public good, but equally important is the need to have our work, and results, critiqued and thereby improved.

As the presentations this morning have shown, the reduction or control of SO_2 emissions from coal combustion--in a cost-effective manner--is a topic of widespread interest today, just as it was at the first symposium on Flue Gas Desulfurization held over 12 years ago. However, a number of the details have changed over the past 12 years. For example, in the earlier years, SO_2 emissions were linked with adverse human health effects, especially those related to respiratory problems. It was chiefly these concerns that resulted in the Clean Air Act of 1970 which led to the State Implementation Plans and the New Source Performance Standards (NSPS's).

More recently SO_2 as well as NO_x emissions have been tied to the problems of acidic deposition--a subject addressed in detail here this morning--and visibility degradation. The problems of acidic deposition have heightened interest in SO_2 and NO_x emissions, not only in the U.S. and Japan but also in Europe. The European community has now joined Japan and the United States in studying and applying commercial applications of flue gas desulfurization (FGD). For example, in the Federal Republic of Germany there are currently 13 installations controlling close to 5,000 megawatts (MW), as well as over 100 installations where the systems have been purchased, but are not yet in operation, representing close to 30,000 MW. It is encouraging to learn of work underway in Europe and Japan and to see so many attendees from other countries at this symposium.

Before focusing on our SO_2 program, I would like to touch on other research we have been conducting on air emission problems from power plants. Research to reduce NO_x emissions has focused on combustion modification. Our major thrust has been to develop the technology for new low-NO_x burners that may be retrofitted to existing boilers or incorporated into new designs. These burners reduce NO_x by delaying the rate of mixing between fuel and air, thereby limiting the availability of free oxygen in the initial burning process.

We are also exploring advanced combustion techniques. Experimentally, two of these "second generation" burners--the distributed mixing burner (for wall-fired boilers) and the rich fireball (for tangentially fired boilers) have shown the potential to reduce NO_x emissions by more than 50% from current NSPS levels for pulverized, coal-fired units.

Coal-fired power plants are also a major source of particle emissions to the atmosphere. Our research on particulate technologies involves cleaning of flue gases subsequent to combustion. Electrostatic precipitators (ESP) are the most commonly used means for controlling the emission of these particles. Fabric filters (sometimes called baghouses) are the major alternative to ESP's for particle control. Both ES[illegible] and fabric filters can achieve greater than 99% particle control.

The major problems with ESP's and fabric filters are their high costs and their operational uncertainties. Our research program in this area is directed toward reducing costs by as much as 50% and minimizing operational uncertainties. Two approaches under development are the use of a multi-stage electrostatic precipitator and electrostatic enhancement of fabric filtration.

The control of SO_2 has also seen improvements over the past decade. In 1973 there were many who questioned the viability of wet scrubbing flue gas desulfurization (FGD) as a means for continuous SO_2 control. Today there are gypsum producing systems, organic acid enhancement, spray dryers, and numerous other technological advances which have led to improved FGD reliability and performance. The questions today, as demonstrated by the papers at this symposium, concern "nitty gritty" issues such as materials of construction, instrumentation, and retrofit factors, all indicative of a maturing technology.

I am pleased to note that the engineering program at EPA has been involved in many of the technological advances in FGD. As commercial applications of FGD have grown, we have continued to seek improvements in the reliability and cost-effectiveness of these processes, through pilot plant studies and cooperative technical assistance arrangements with private industry. Examples of these efforts are the evaluation of an organic acid-enhanced, limestone FGD system with the San Miguel Electric Cooperative in Jourdanton, Texas, which will be discussed in one of the sessions this afternoon; and field testing of pilot and commercial scale spray drying FGD systems at facilities in a number of states, which is the subject of the session on Thursday afternoon. Despite our past efforts, and those of other Federal agencies such as the Department of Energy and the Tennessee Valley Authority, as well as those of private industry, including EPRI, the costs of SO_2 control remain high relative to NO_x and particulate control.

For this reason we are continuing to conduct research to develop higher reliability and lower cost SO_2 emission reduction methods. Through our in-house pilot plant program, we are focusing on spray drying FGD--particularly on reducing costs, such as the use of cheaper or more reactive sorbents. The overall objective of this work is to develop improvements to spray drying FGD which can easily be field tested and commercialized by private industry.

Although emphasis in the program is being placed on reducing SO_2 control costs, combined SO_2/NO_x and SO_2/particle emission approaches are also being evaluated. We are developing several innovative concepts in SO_2 control which will offer low-cost options for acidic deposition reduction in the event proposed legislation calling for this reduction becomes law. Our largest effort among these combined emission reduction technologies is demonstration of the technology generally known as LIMB (limestone injection combined with low-NO_x multistaged burners). Those of you who attended the last FGD symposium over 18 months ago were introduced to this concept through presentations by EPA, EPRI, and the L. & C. Steinmuller Co. of West Germany. The LIMB concept today no longer is limited to injection of limestone through the burners; it also can involve injection of specially calcined, high surface area lime, or other alkaline materials, at different locations in the boiler in order to optimize the SO_2 capture. By late 1986 or early 1987, we plan to have a commercial demonstration of the LIMB technology in operation on a wall-fired unit at Ohio Edison's Edgewater Station.

Another approach to lower cost technology is one that combines SO_2 control with particle emission control. It is a concept we have developed that involves spray drying in a modified electrostatic precipitator; this concept has been dubbed "E-SOX." The first step in the E-SOX concept involves replacing the existing electrodes in the second and third sections of a conventional 3-section ESP with larger diameter electrodes and installing cold pipe prechargers at the entrance to each section, thereby converting the latter sections into a multistage ESP. The second step in this approach involves complete removal of the electrodes and plates in the first section and installing spray headers for introduction of alkaline solution or slurry for SO_2 removal. The prechargers and larger diameter electrodes installed in the latter ESP sections allow the ESP to operate at higher particle removal efficiency than previously, while at the same time making free space available for the spray headers.

Limited pilot testing has shown that moderate to high SO_2 removals may be expected using this concept, depending on the alkaline solution used. Additional tests are planned in the future. The major advantage of this approach is that it involves no changes to existing ductwork or special vessels for spray drying. For this reason it could be easily retrofitted to ESP's on existing coal-fired units. The E-SOX concept will be discussed further in the session on Thursday morning.

In addition to our hardware-related control technology research, we have a continuing effort to assess the performance and engineering costs of both commercial and emerging technologies. These efforts have become more prominent as our involvement in the National Acid Precipitation Assessment Program has increased. The Advanced Utilities Simulation Model or AUSM mentioned earlier this morning by Dr. Rubin is being developed by the University of Illinois under this national program. The AUSM contains cost algorithms which originated in earlier EPA engineering cost modeling efforts. Further improvements in the AUSM cost algorithms are planned, particularly in determining site-specific retrofit factors for the various emission control technology options.

Finally, one of the major efforts in our engineering program has been what many refer to as "technology transfer." This is simply our way of disseminating data and information from technological developments by EPA and others via published papers, technical reports, industry briefings, and symposia such as this. Over 3 years ago, we joined forces with EPRI in continuing the FGD symposium series. This joint sponsorship has, we believe, been highly successful in making these meetings more responsive to the needs and interests of those who need this data and information in their work, particularly the users of FGD technology. We also benefit from the other work discussed at these symposia and your comments and constructive criticism of our program.

As with any major research effort, we in EPA cannot do all the necessary work ourselves. Close cooperation is needed between our researchers and those of you in other organizations doing research in the field, as well as with the user community. Mutual discussion and constructive criticism are crucial in meeting our common objective: To improve the reliability and reduce the costs of pollution control. Furthermore, we strongly believe that improving the environment and maintaining the economic vitality of the nation are not mutually exclusive goals. They are two worthy, achievable goals toward which we must all work. I leave this challenge with you.

Session 3: LIMESTONE FGD/ORGANIC ACID ENHANCEMENT

J. David Mobley, Chairman
U.S. Environmental Protection Agency
Research Triangle Park, NC

RESULTS OF USING ORGANIC ACID IN SAN MIGUEL ELECTRIC'S FLUE GAS DESULFURIZATION SYSTEM

Prepared by:

Jack M. Burke
Radian Corporation
Austin, Texas 78766

Robert Cmiel
San Miguel Electric Cooperative
Jourdanton, Texas 78026

and

J. David Mobley
Air and Energy Engineering Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

ABSTRACT

This paper summarizes San Miguel Electric Cooperative's first full year of operation after conversion of the Unit 1 flue gas desulfurization (FGD) system to an organic acid enhanced limestone system. Plant operating data from 1983 (without organic acid addition) and 1984 (with organic acid addition) were reviewed. Based on that review, changes which occurred once organic acids were added to the system were identified and cost savings resulting from those changes estimated. The cost estimates showed that savings directly attributable to organic acid use exceeded the cost for organic acid by $109,000 in 1984. Further, additional cost benefits resulting from organic acid use may have been in excess of $3 million. Because of this positive experience, San Miguel continues to use organic acid in the FGD system.

INTRODUCTION

Over the period November 1983 to March 1984, a series of parametric tests were conducted to evaulate the economics of converting San Miguel Electric Cooperative's limestone flue gas desulfurization (FGD) system to an organic acid enhanced limestone FGD system. The parametric test program was sponsored by the Air and Energy Engineering Research Laboratory of the Environmental Protection Agency in cooperation with San Miguel. Radian Corporation was responsible for conducting the tests.

Prior to the tests at San Miguel, organic acids[1] had been successfully tested at two full-scale FGD systems to enhance the performance of existing absorbers. At both Springfield City Utilities' Southwest Power Plant and Central Illinois Lighting Company's Duck Creek Station, organic acid additives are currently being used to help bring the FGD systems into compliance with SO_2 emission regulations. These applications have established organic acids as additives which could enhance the SO_2 removal performance of limestone FGD systems.

The organic acid addition tests which were conducted at San Miguel had a different objective. These tests marked the first time organic acid additives were being evaluated on a strictly economic basis. At San Miguel, the FGD system was in compliance with the 1.2 lb $SO_2/10^6$ Btu[2] emission standard prior to the use of any organic acid additive. However, the plant was maintaining compliance with the standard at the expense of very high limestone consumption rates (i.e., poor reagent utilization). In 1983, San Miguel's limestone utilization[3] averaged 70 percent. If this could be increased to 90 or 95 percent, a significant cost savings would be realized.

In the parametric tests conducted at the San Miguel plant, the effects of organic acids on FGD system performance were quantified over a range of operating conditions. The results of these tests showed that addition of organic acid (specifically DBA) provided flexibility in selecting process operating conditions while still maintaining compliance with SO_2 emission regulations. This in turn resulted in improved process operation and reduced limestone consumption.

---

[1] Specifically, adipic acid and DBA (dibasic acid) which is a byproduct of adipic acid manufacture. DBA contains adipic, succinic, and glutaric acids. Generally, any organic acid which buffers in the pH range of 3 to 6 can be used to improve SO_2 removal in an FGD system.

[2] It is EPA policy to report measurements in SI units. However, because of convention in the electric utility industry, this paper uses British engineering units. A table of conversion factors is attached.

[3] Utilization = (moles SO_2 removed) / (moles $CaCO_3$ added) x 100 percent.

Economic projections based on the results of the parametric test program indicated that San Miguel could reduce the operating costs of the Unit 1 FGD system by over $600,000 in 1984 [1]. Also, a net present worth analysis of organic acid use over 15 years showed an estimated savings of $7.2 million in 1984 dollars. In addition to the projected cost savings, there were other benefits expected from conversion of the system to organic acid use including the ability to operate the unit at higher loads and the potential for reducing station power use. Because of these projected savings in operating costs, San Miguel installed and currently operates a permanent organic acid addition system for the Unit 1 FGD system.

This paper presents an update of the economic projections which were based on the relatively short parametric test program. The information presented here is based on a review of operating and financial data from San Miguel's first full year of operation with the organic acid enhanced limestone FGD system. Year-to-year comparisons between 1983 (without organic acid addition)[1] and 1984 (with organic acid addition) are provided. Some of the major factors included in the updated economic analysis are organic acid consumption rates and limestone utilizations which are based on annual averages. The discussion of results also includes comparison of FGD system maintenance expenditures, plant heat rates, and plant generating rates for 1983 and 1984.

PLANT DESCRIPTION

San Miguel's Unit 1 is a 400[2] MW lignite fired boiler located in Atascosa County outside of Jourdanton, Texas. The plant is a mine-mouth facility firing a high-sulfur (about 2 percent), high ash (about 20 percent), low heating value (about 5600 Btu/lb) Texas lignite. Under federal and state law, the plant is required to operate an air quality control system consisting of an electrostatic precipitator for particulate collection, followed by a wet limestone FGD system for SO_2 removal. The FGD system was designed to meet an emission limit of 1.2 lb $SO_2/10^6$ Btu which corresponds to about 85 percent SO_2 removal at 2700 ppm SO_2 inlet concentration.

The San Miguel Unit 1 FGD system was designed and supplied by Babcock & Wilcox . It consists of four quench-absorber modules (three operating and one spare), two 115-ft diameter thickeners, thickener underflow and overflow storage tanks, a limestone feed preparation system, and a solids dewatering and disposal system. Figure 1 is a schematic of the FGD system which shows one of four identical absorber modules. Two boiler ID fans exhaust flue gas to a common plenum which supplies the scrubber modules. Any of the modules can be isolated from the flue gas path by closing inlet and outlet dampers. In addition, there is a flue gas bypass which can be used if emissions drop below the 1.2 lb $SO_2/10^6$ Btu limit. Since flue gas exiting the scrubber is

---

[1] The final 6 weeks of 1983 did include operation with organic acid additives.

[2] Maximum guaranteed load is 401 MW and maximum expected load is 437 MW [2].

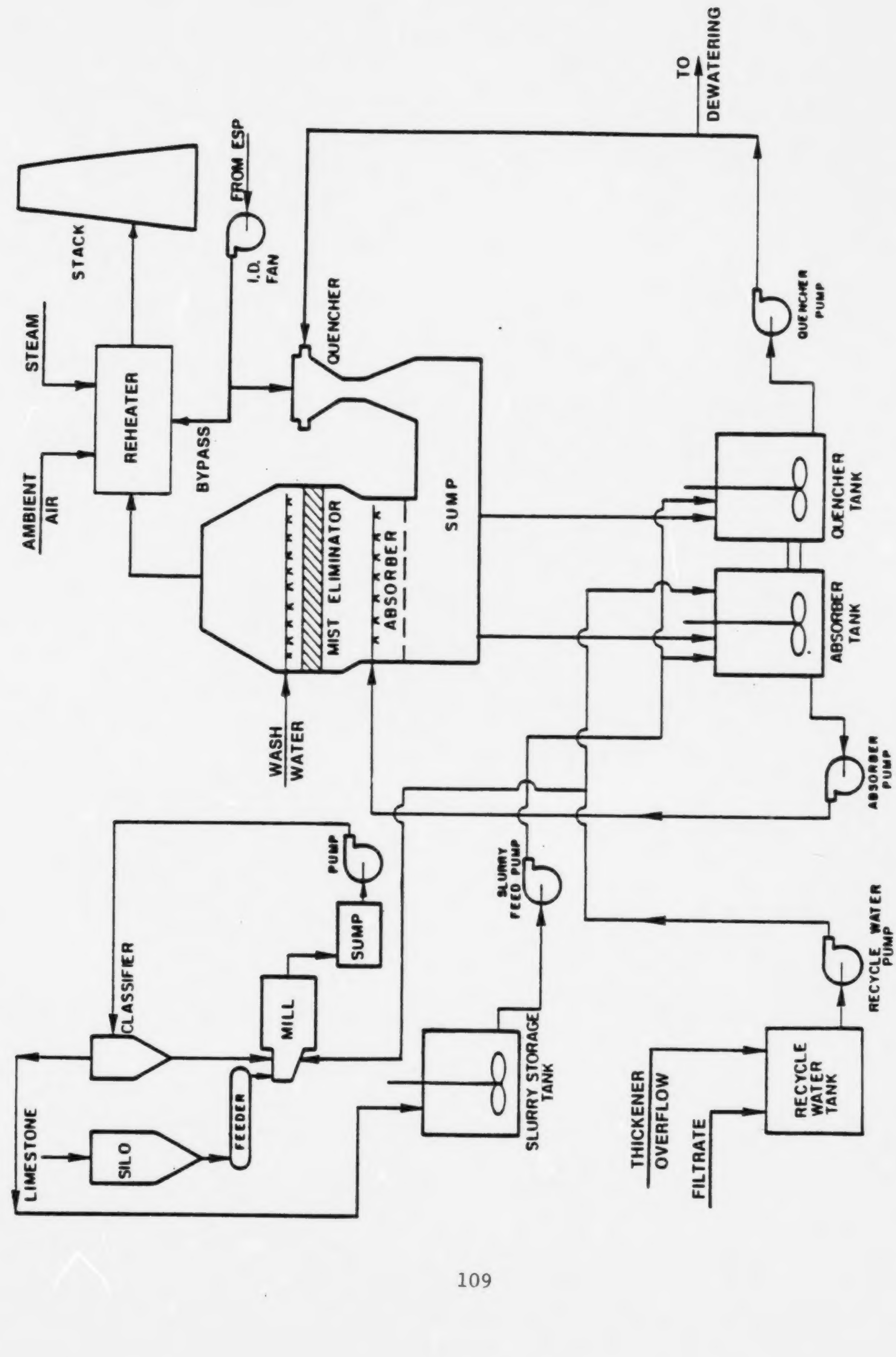

STACK
FROM ESP
I.D. FAN
STEAM
AMBIENT AIR
REHEATER
BYPASS
QUENCHER
MIST ELIMINATOR
ABSORBER
SUMP
WASH WATER
TO DEWATERING
QUENCHER PUMP
QUENCHER TANK
ABSORBER TANK
ABSORBER PUMP
LIMESTONE
SILO
FEEDER
CLASSIFIER
MILL
SUMP
PUMP
SLURRY FEED PUMP
SLURRY STORAGE TANK
RECYCLE WATER PUMP
RECYCLE WATER TANK
THICKENER OVERFLOW
FILTRATE

Figure 1. San Miguel FGD System.

reheated to a constant temperature (175°F), hot flue gas bypass reduces the load on the reheat system and, therefore, increases overall plant efficiency. Gas bypass also reduces pressure drop through the absorbers (at constant load) which would be expected to reduce the power required to operate the two axial flow ID fans.

Flue gas which enters the absorbers (about 1,500,000 acfm) first passes down through a venturi-type quench tower where the gas contacts sprays of recirculating slurry. There, the gas is saturated with water and some SO_2 is removed. The gas then turns 180° and passes up through a perforated-tray absorber tower where it is again contacted with a recirculating slurry of calcium sulfite/sulfate and limestone. There, the majority of the SO_2 removal occurs. The flue gas then leaves the absorbers and passes through a two-stage Chevron-type mist eliminator before entering a reheat chamber common to all four modules. The scrubbed flue gas is mixed with bypassed flue gas and with ambient air which has been heated to 400°F by steam coils. After the flue gas is reheated, it enters the stack and is discharged to the atmosphere.

Limestone reagent for the FGD system is ground and slurried in a ball mill, classified in a hydrocyclone circuit, and discharged to a storage tank. Slurry from storage is then fed to the absorber and/or quench recirculation tanks to maintain the pH in these tanks at set levels. The limestone feed and pH control system is designed so the pH in the absorber and quench loops can be controlled independently (within certain limits). Overall slurry flow in the system is such that it cascades from the absorber recirculation tank to the quench tank. Slurry from the quench loop is continuously blown down to the thickeners for dewatering and eventual disposal. With this slurry flow scheme, the limestone utilization in the quench recirculation tank represents the overall limestone utilization for the FGD system.

PARAMETRIC TEST RESULTS

The major factor which made San Miguel a good candidate for reducing operating costs through the use of organic acid additives was the excessive quantity of limestone being used to keep the plant in compliance. Not only does this result in higher costs for raw limestone, but costs are incurred to grind and classify the excess limestone on the front end and to dewater and dispose of unreacted limestone on the back end of the FGD system. Because limestone utilization is so important, one major objective of the parametric test program was to quantify the trade-off between organic acid (specifically DBA) consumption (which increases with increasing concentration) and limestone utilization. This trade-off exists because higher DBA concentrations permit operation at lower pHs which in turn results in improved limestone utilization.

Tests were conducted over a range of organic acid concentrations from about 500 to 2000 ppm. The results showed that, at an organic acid concentration of approximately 600 ppm, pHs in the FGD system could be reduced from over 6.0 to 5.4 in the quench loop and 5.8 in the absorber loop. Operation at these pHs resulted in an overall limestone utilization of over 90 percent. Further, even at the lower pHs, SO_2 removal was high enough to permit San Miguel to bypass between 5 and 10 percent of the boiler flue gas around the absorber modules at a load of 420 MW. This reduced gas velocities in the absorber which, in combination with the reduced operating pHs, eliminated mist eliminator plugging. The flue gas bypass also reduced the requirements for reheat steam which provided an additional cost savings.

The parametric test results were also evaluated to determine if further cost savings could be realized at the higher DBA concentrations tested. That evaluation indicated that, on a short-term basis, quantifiable cost savings did not offset the costs associated with the increased consumption of DBA which occurs at higher concentrations. Since limestone utilization had already been increased to above 90 percent, there was little additional benefit from operating at the higher utilizations which were possible at higher organic acid concentrations. And although additional flue gas bypass was possible, the reduced requirement for reheat steam was not enough to offset the costs associated with increased DBA consumption.

The preceding discussion summarizes the major results of the parametric tests and subsequent economic analysis completed as part of the original San Miguel study. Based on the original study, San Miguel was provided with guidelines for operation of the organic acid enhanced limestone FGD system.

1984 OPERATING RESULTS

Following the parametric test program, the organic acid addition system was turned over to plant operations at San Miguel. No test personnel were on site to track operation of the system. Therefore, in order to evaluate the long-term results from 1984, overall measures of FGD system performance were reviewed. The primary sources of information for this review were San Miguel's Monthly Generation and Monthly Fuel reports from 1983 and 1984. Items of importance in these reports included fuel analyses, limestone consumption rates, station power use, and plant generating rates. Other plant records were examined to determine FGD system maintenance costs and average organic acid use rates and concentrations in the FGD system.

The discussion which follows summarizes significant 1984 operating results for the San Miguel organic acid enhanced limestone FGD system. Areas of interest include:

- DBA consumption rate,
- pH and limestone utilization,
- Plant generating rate,

- Plant heat rate and station power use, and
- FGD system maintenance requirements.

Where appropriate, these results are compared with data from 1983 and/or results from the EPA sponsored parametric test program.

DBA CONSUMPTION RATE

A major factor affecting the costs of operating the San Miguel FGD system with organic acid addition is the consumption rate of DBA. Since the costs for the DBA represent the only significant operating expense associated with acid addition, it is important to have an accurate estimate of the DBA consumption rate. Therefore, one objective of the parametric tests at San Miguel was to quantify the DBA consumption rate as a function of concentration in the recirculating slurry. This was done by completing DBA material balances on the scrubber system and measuring the loss rate by difference using:

Loss Rate = Addition Rate - Accumulation Rate

With this approach, the different mechanisms for DBA consumption -- including precipitation, degradation, and loss in the liquid phase of the disposed sludge -- were not quantified individually.

Since the parametric tests were of relatively short duration (1 week or less), the measured DBA consumption rates did not necessarily represent long-term consumption rates. Therefore, one item of interest in evaluating San Miguel's 1984 operating data was to determine how accurately the DBA consumption rates measured in short-term tests reflect the actual long-term experience at the plant.

Figure 2 compares the consumption rate data gathered during the parametric tests with the DBA consumption measured at San Miguel over the period June 1 to December 31, 1984. (This period was selected since it represents the start of operation after the parametric tests and the annual plant outage which ended in May.) The curve shown in the figure represents the parametric data while the single point represents the average of 7 months of operation. As shown, the long-term DBA consumption rates agree very well with the parametric test results. In this case, the favorable comparison between the actual experience and the test results suggests that the parametric test approach accurately quantified long-term consumption rates.

pH AND LIMESTONE UTILIZATION

The other factor which had a major impact on the economics of converting the San Miguel FGD system to organic acid addition is the limestone utilization which could be achieved once organic acid was added to the system. In 1984, the limestone utilization increased to just over 82 percent from 70 percent in 1983. As will be discussed later, this improvement in utilization more than offset the costs for organic acid in 1984. It

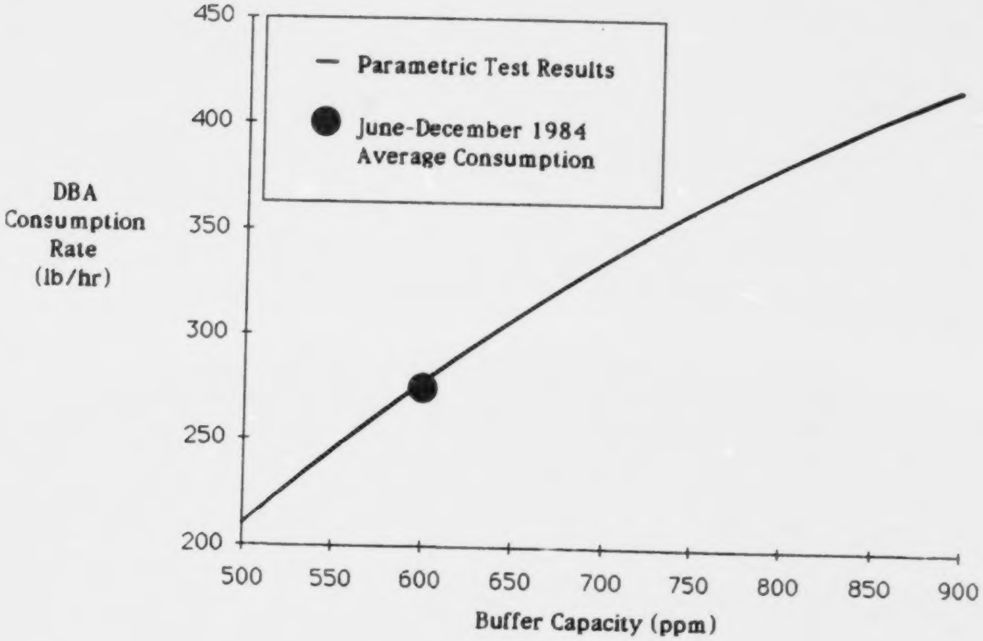


Figure 2. DBA Consumption vs. Buffer Capacity.

should be noted, however, that the change in utilization between 1983 and 1984 represents only two-thirds of the improvement which the parametric tests indicated should be possible. This indicates that it may be possible for San Miguel to realize additional savings by further improving limestone utilization in the future.

PLANT GENERATING RATE

Another important change between operation in 1983 and 1984 was the ability to bypass flue gas around the FGD system. As mentioned earlier, the parametric test results indicated that between 5 and 10 percent flue gas bypass was possible at the recommended DBA concentration and operating pHs in the FGD system. As a result of bypassing flue gas, the pressure drop downstream of the axial flow ID fans was reduced. An alternative way to view this change is that, with gas bypass, it becomes possible for the ID fans to move more flue gas at the same pressure drop. For San Miguel, this change meant that it was now possible to operate the unit at a higher load more frequently. Over a period of months, plant operating personnel found that higher gas bypass rates helped maintain operation at higher loads[1]. Additional bypass (above 10 percent) was obtained while maintaining compliance with SO_2 emission regulations by increasing the operating pH in the absorber and quench loops. This operation at higher pHs (up to 6.0 in the quench loop) caused San Miguel's 1984 limestone utilization to fall below the 90 percent level which the parametric tests indicated should be possible.

---

[1] Bypass was possible when low sulfur coal was being fired prior to organic acid addition. With organic acid addition, bypass became continuous.

Figure 3 compares 1983 and 1984 load distributions as a function of operating time for San Miguel's Unit 1. As shown, the unit spent a larger fraction (about 15 percent) of operating time at loads below 400 MW in 1983 compared to 1984. Conversely, the unit operated at loads above 430 MW for about 15 percent more time in 1984. This shows that operation at loads above 430 MW accounted for all of the increased time at higher load in 1984. On the average, the unit operated at a 15 MW higher load in 1984 (414 MW in 1984 vs. 399 MW in 1983).

While there are a number of factors which may have contributed to the shift to higher load operation in 1984, San Miguel attributes much of this increase to the reduced backpressure on the boiler ID fans made possible with increased flue gas bypass. Unfortunately, San Miguel's "Unit Status Report" (which details reasons for load changes) does not identify what factors limit boiler load. Therefore, it is not possible to quantify what fraction of the increased operating time at higher load is a direct result of increased flue gas bypass.

In terms of costs, San Miguel has traded the small, but quantifiable cost savings associated with reduced limestone consumption for the large increase in revenues which results from generating more power. Specifically, 1984 revenues for Unit 1 increased by $11.1 million over 1983. Approximately $4.3 million of this increase resulted from operating at a higher average load in 1984 while the balance can be attributed to operating the plant for more hours in 1984. Although the fraction of the increased revenues which can be attributed to the ability to bypass more flue gas cannot be quantified, it appears that a large cost benefit resulted.

PLANT HEAT RATE AND STATION POWER USE

Two operating overheads which were reduced by the conversion of the San Miguel FGD system to an organic acid enhanced system are:

- The plant heat rate, and
- The fraction of generated power required to run the plant.

Plant heat rate was reduced because flue gas bypass reduces the requirement for reheat steam in the FGD system. At 10 percent bypass and a load of 420 MW, heat balance calculations show the plant heat rate will be reduced approximately 50 Btu/kWh when compared to operation without flue gas bypass.

The station power use was also reduced as a result of the conversion of the FGD system to using an organic acid additive. There were several factors which contributed to this reduction including:

- Reduced ball mill operation (due to the improvement in limestone stoichiometry),

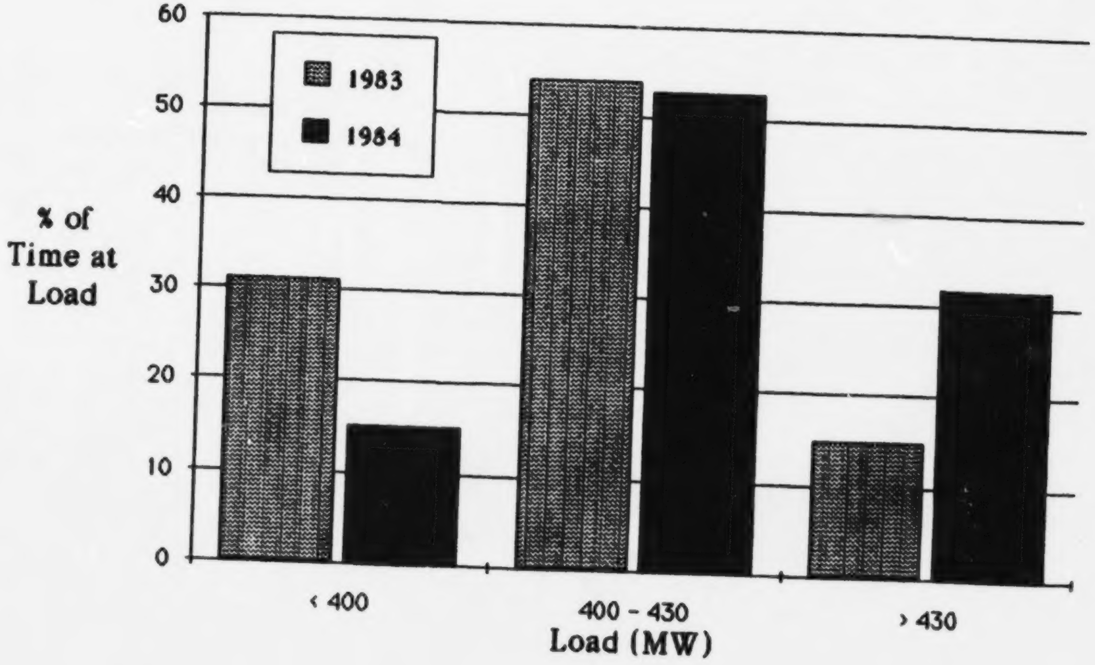


Figure 3. San Miguel Load Distribution

- Reduced operation of the dewatering equipment (due to less limestone being present in the waste sludge), and

- Reduced power demand by the boiler ID fans (due to the decreased pressure drop across the FGD system resulting from flue gas bypass).

The total reduction in station power use in 1984 is estimated to be approximately 1.4 MW at full load. This corresponds to a reduction of about 4.5 percent in San Miguel's 1983 station power use (which totaled approximately 8.9 percent of power generated). With other things being equal, the expected reduction in station power use should be evident in a comparison of 1983 and 1984 averages. However, there was essentially no difference in the average station power use between 1983 and 1984 at comparable unit loads. The reason for this result is not clear. It is likely that power demands in other areas of the plant increased slightly and offset the decrease resulting from more efficient operation of the FGD system.

FGD SYSTEM MAINTENANCE REQUIREMENTS

During the short-term parametric tests, the tendency of the absorbers and mist eliminators to plug and/or scale appeared to have been reduced. In the case of the absorbers, this change was attributed to operation at lower pHs while the improvement in mist eliminator operation was attributed to both reduced absorber operating pH and reduced gas velocity in the absorber tower.

A review of FGD system operation in 1984 shows that:

- The mist eliminators no longer experience any scaling or plugging. In fact the system operated throughout 1984 without any manual cleaning of the mist eliminators. This is likely a result of continued operation with flue gas bypass.

- San Miguel continues to have problems with absorber scaling which requires manual cleaning of each module approximately once a month. The continuation of this problem is, in part, attributable to San Miguel's continued operation at pHs above 5.8 in the absorber.

Since manpower for cleaning the mist eliminators was eliminated in 1984, the annual maintenance expenditures for 1983 and 1984 were compared to quantify the savings in maintenance costs which resulted. This comparison showed no change in FGD system maintenance costs in the 2 years. 1983 costs were $1.33 million, and 1984 costs were $1.35 million. Apparently, the personnel previously employed to clean the mist eliminators are now being employed in other maintenance jobs around the FGD system. This represents an improvement in system operation, but not a direct cost savings.

1984 COST SAVINGS

One very important aspect of San Miguel's experience with organic acid addition is the reduction in operating costs realized in 1984. The discussion which follows presents estimates of the 1984 cost savings. The approach which has been used to define the reduction in FGD system operating costs is to provide two estimates. The first quantifies savings which can be directly attributed to organic acid use (e.g., improved limestone utilization) while the second identifies limits for cost savings which could not be quantified in reviewing the 1984 operating data (e.g., the ability to operate at higher loads).

DOCUMENTED SAVINGS

Table 1 presents a summary of the cost savings which can be directly attributed to organic acid use at San Miguel in 1984. This table shows that the documented cost savings totaled just over $100,000 which represents nearly half of the Electric Cooperative's "net operating margin" for 1984 [3]. The actual savings resulting from improved limestone utilization was $362,000 which more than offset the $306,000 cost for organic acid. Table 1 also shows that an additional $53,000 savings resulted from reduced limestone grinding and dewatering costs in 1984. These savings are a direct result of the reduction in the limestone consumption which was achieved by San Miguel in 1984.

TABLE 1. DOCUMENTED 1984 COST SAVINGS

Cost Item	Savings ($1000s)
Organic Acid	($306)
Limestone Reagent	$362
Limestone Grinding	$37
Dewatering	$16
Total	$109

ESTIMATED SAVINGS

While the documented cost savings from organic acid use at San Miguel were just over $100,000 in 1984, operating changes (made possible with organic acid use) resulted in other cost benefits which far outweigh the documented savings. Unfortunately, the fraction of these other benefits which are directly attributable to organic acid use could not be quantified with the operating data collected by San Miguel. It is, however, possible to provide an estimate of the maximum dollar value of these additional savings.

Table 2 presents estimates of the maximum savings from operational changes which are in part attributable to use of organic acid in the San Miguel FGD system. As shown, the potential value of these savings is over $3 million which is much greater than the documented savings. The discussion which follows examines each item in Table 2 in more detail.

TABLE 2. ESTIMATED MAXIMUM 1984 COST SAVINGS

Cost Item	Savings ($1000s)
Flue Gas Bypass	$275
Reduced Fan Power	$287
Increased High Load Operation	$2727
Total	$3289

Flue Gas Bypass

As discussed earlier, San Miguel found it advantageous to operate at higher flue gas bypass rates than could be attained at the operating conditions recommended based on the parametric test program. This reduced FGD operating costs by reducing the requirement for reheat steam, but it is not certain how much costs were reduced since San Miguel has no direct measure of the flue gas bypass rate. During the parametric test program, bypass rates as high as 12 percent were measured at high organic acid concentrations (a situation similar to the high pH operation in 1984). Assuming an average bypass rate for 1984 of 10 percent, this translates to a savings in fuel costs of $275,000 or nearly three times the documented savings. It also means that the boiler-turbine-generator system was capable of producing over 2 MW more electricity at the same firing rate. It is likely this also contributed to operation at higher boiler loads in 1984.

Reduced Fan Power Requirements

Another benefit of flue gas bypass is the reduced power required by the boiler ID fans at reduced scrubber pressure drop. San Miguel has observed a reduction in power required by the two ID fans which is estimated to be 100A at 7200V or approximately 1 MW. Assuming this power can be sold instead of consumed in the plant, it has a value equal to San Miguel's sales price for power (38.6 mills/kWh in 1984). This translates into annual savings of $287,000 in 1984 (7450 hrs operation).

Plant Generating Rate

As mentioned earlier, Unit 1 operated at a 15 MW higher average load in 1984. This change was responsible for increasing San Miguel's revenues by $4.3 million. Since San Miguel is a cooperative, a profit value is not attached to this additional revenue (profits are rebated to customers), but it is apparent that operation at higher load had a significant impact on San

Miguel's delivered cost of power. In order to put this savings on the same basis as other savings, it is necessary to assign a "profit margin" to the generation of incremental power. Assuming that this incremental power was generated without incurring additional fixed charges (i.e., capital expenses, taxes, interest, and insurance), the margin on the additional power would be the ratio of generating costs (14.1 mills/kWh) to the sales price of the power (38.6 mills/kWh) or about 63 percent. As shown in Table 2, this assumption translates the value of additional power into a cost savings of $2.7 million.

CONCLUSIONS

There are several conclusions which can be drawn from this review of San Miguel's 1984 operation using organic acid.

- At San Miguel, operation with organic acid resulted in a significant reduction in FGD system operating costs in 1984. The documented savings which resulted from process changes which were made possible after organic acid was added to the system more than offset the costs of the organic acid raw material. Further, the maximum value of estimated savings from organic acid addition makes organic acid use even more attractive. Based on their 1984 experience, San Miguel will continue to use DBA to enhance the Unit 1 FGD system performance.

- Operation with organic acid helped the plant operate at higher loads for longer periods of time in 1984 compared to 1983. The amount of this change which can be directly attributed to use of organic acid could not be documented. However, additional revenues of $4.3 million resulted from operation at higher loads.

- The San Miguel FGD system was operated at conditions (i.e., pHs as high as 6.0) other than those recommended after the parametric test program. It is likely that some additional cost savings can be realized by searching for economically optimum operating conditions and including the ability to operate at higher loads as a factor in the economic analysis. Trade-offs which must be considered include organic acid concentration, pH, flue gas bypass rate, and boiler load limits. The additional savings from such an evaluation could be as much as $300,000 per year.

Overall, San Miguel has had a very positive experience using organic acid to improve the operation of their FGD system. The plant was able to generate more power in 1984 compared to 1983. Also, since in 1984, documented savings have more than paid for the organic acid used, the utility plans to continue operating the FGD system with organic acid addition.

REFERENCES

[1] Burke, J.M., Technical and Economic Evaluation of Organic Acid Addition to a Commercial FGD System, EPA-600/7-85-014 (NTIS No. PB85-191724), Radian Corporation, Austin, Texas, April 1985.

[2] San Miguel Fact Sheet (Appendix B) in Proceedings: EPA's Industry Briefing on the Organic-Acid-Enhanced Limestone FGD Process (July 1984), EPA-600/9-85-009 (NTIS No. PB85-181105), March 1985.

[3] San Miguel Electric Cooperative, Inc., 1984 Annual Report.

CONVERSION FACTORS

To Obtain	Multiply	By
m^3/sec	10^3 ft^3/min	0.4719
kg	lb	0.4536
ng/J	lb/10^6 Btu	429.9
°C	(°F - 32)	0.5556
J/kg	Btu/lb	2326
m	ft	0.3048
J	Btu	1055.1
Metric Tons	Tons	0.907

State-of-the-Art Design Applications on a Closed-Loop FGD System

by:

Dennis Laslo and Even Bakke

Peabody Process Systems, Inc.
201 Merritt 7, Corporate Park
Norwalk, CT 06852

ABSTRACT

Seminole Electric Cooperative's Unit 1 and Unit 2 in Palatka, Florida are capable of 1240 MW of generating power. The limestone-based flue gas desulfurization systems for both boilers incorporate an organic acid addition system for operation at high dissolved salt concentrations, and, on Unit 1, a unique double draw-off crystallizer unit operation for improved cake dewatering, and a two-tank forced oxidation system for production of gypsum.

Discussions will include full scale closed-loop water management and operating experience, results from a commercial gypsum dewatering pilot plant, the results of double draw-off product removal on both calcium sulfite and calcium sulfate crystals, and, operating experience and economics of organic acid addition. Also, the results of a successful test of sodium thiosulfate addition as a gypsum scale inhibitor will be presented.

INTRODUCTION

In recent years, several developments in flue gas desulfurization (FGD) technology have promised improved system performance, but have not been implemented in new FGD systems. These include the use of organic acids to counteract the effects of high concentrations of dissolved salts (1,2,3,4), the use of oxidation inhibitors, such as sodium thiosulfate, for unsaturated operation (5,6,7), and the incorporation of crystallization technology into an FGD system for improved dewatering (8,9).

All of these technologies have been successfully implemented at the Seminole Electric Cooperative, Inc. (SECI) FGD system and will be discussed in detail in this paper.

SECI SYSTEM DESCRIPTION

SECI operates two 620 MW boilers, Unit 1 and Unit 2, each equipped with an FGD system designed and constructed by Peabody Process Systems, Inc. (PPSI), and a sludge fixation system, designed and constructed by CSI. The fuel used is a washed, high sulfur (3%), high chloride (0.3%) Kentucky coal. Typically, coal washing removes approximately four percent of the sulfur, while the FGD system removes the remaining 86 percent, meeting the overall 90 percent NSPS (rolling average) requirement.

The limestone-based FGD system consists of four operating spray tower modules and one spare for each boiler unit. Each module typically has three operating pumps and two spares. Each unit has an organic acid addition system and Unit 1 is equipped with an in-situ forced oxidation system and a classified product removal system.

Waste slurry from the FGD system is fed to the CSI dewatering and stabilization system. This consists of three 100 percent capacity thickeners, six 25 percent drum filters and two 100 percent stackers (10). Four multi-million gallon emergency ponds are used to accept liquor when servicing a thickener, or other large tank and also collect landfill runoff and rainwater. The ponds also act as capacitance for excess liquid inventory.

OPERATING EXPERIENCE

INITIAL OPERATION

SECI had a start-up not typical of the industry (10) as there were significant turbine problems during the first nine months, preventing tuning of the FGD system. After the turbine problems were rectified, several problems were experienced in the FGD system:

1) The use of an explosive with a plastic overwrap in the limestone quarry introduced the plastic and other tramp material into the FGD system. The material clogged wash nozzles and resulted in significant plugging of underwashed areas inside the absorber modules, especially the mist eliminators. This problem was eventually minimized by installation of additional strainers and more frequent strainer cleaning.

2) Severe scaling was experienced in the mist eliminator and other areas of the FGD system. Peabody contracted Acurex Corporation to perform extensive tests of the FGD chemistry. It was determined that an erratic fresh water makeup rate was causing periods of extreme gypsum supersaturation when the ball mill was not operating. Large quantites of additional supernate are required when the ball mill is operating. In order to also supply wash liquor to the absorbers, the supernate used in the ball mill is automatically replaced with makeup water, resulting in excess liquid inventory addition to the reagent storage tank. As this excess liquid inventory is later fed to the system (when the ball mill is not operating), the thickeners overflow to the emergency pond, and very little makeup water is added. This sawtooth pattern of fresh water addition resulted in periods of severe gypsum supersaturation during the time when the ball mill was not operating and fresh water demand was low.

3) Severe mist eliminator plugging was experienced a second time, this time accompanied by severe scaling. At the same time, it was discovered that a depression in maximum system pH had occurred, preventing proper pH control. SO_2 removal efficiency had slowly dropped from over 90 percent to under 85 percent. Again, detailed chemical analyses were performed to isolate the problem. In addition, the mist eliminator blade spacing was increased to improve irrigation. Tests for limestone blinding were negative, however the chloride concentration had increased to a level over 10,000 mg/l. The limestone stoichiometry was also extremely high due to the improper pH control. These two factors with the aforementioned erratic makeup water rate are believed to have been the cause of the plugging/scaling. In addition, the lower operating pH increased natural oxidation and therefore, gypsum supersaturation. The solution

to these problems will also be discussed in greater detail later in the paper.

CLOSED LOOP OPERATION

In a truly closed loop FGD system, all dissolved salts exit the system in the filter cake. Since substantial quantites of water are evaporated by saturation of the hot flue gas, dissolved salts can reach very high concentrations, especially when high chloride coal is burned. The FGD and sludge fixation systems at SECI are both constructed on concrete pads with spill-containing curbs, resulting in an extremely "tight" closed-loop system. The combination of a tight closed-loop and high chloride coal resulted in the accumulation of dissolved chloride ions (Cl^-) to unprecedented levels (11) - as high as 38,000 mg/l.

The effect of dissolved salts, primarily calcium chloride ($CaCl_2$), have been studied extensively in pilot plants (1,2,3,4,12). Results have shown a significant decrease in SO_2 removal, a decrease in recycle tank equilibrium pH, and an increase in the gypsum saturation levels (or scaling potential), as the dissolved $CaCl_2$ concentration increased.

At SECI, Cl^- concentrations have typically ranged from 18,000 to 25,000 mg/l. The recycle tank equilibrium pH response to Cl^- accumulation was identical to the response experienced in the pilot plant work. The result was a depression in the maximum obtainable pH to 5.4-5.6 (from over 6.0). This pH limit prevented proper operation of the automatic pH control (since the controller set-point was higher than the equilibrium pH) and excessive reagent was added. In order to properly add reagent to the FGD system, the pH set-point was lowered from the design point of 5.8 to a few tenths of a pH unit below the calculated equilibrium pH (5.0 to 5.4). This allowed proper reagent addition but severely reduced SO_2 removal efficiency.

NEW DESIGN APPLICATIONS

DBA - A COUNTERMEASURE FOR CHLORIDES

Organic acids have been thoroughly studied as an economical mass transfer enhancement additive (13,14,15,16,17) in FGD systems. Previous pilot plant studies (1,2,3,4) had indicated that small quantities of organic acids, such as adipic acid or an organic acid waste stream, commonly called dibasic acid (DBA), counteract the negative effect of chlorides on SO_2 removal efficiency. A two week test program was designed to examine the effect of DBA as an additive to improve the SO_2 removal efficiency, to determine the required DBA concentration required, and the actual DBA degradation rate at SECI.

The results, shown in Table 1 indicate that less than 600 ppm of DBA, with three operating recycle pumps, was required to overcome the effects of chlorides (at the time of the test, the Cl^- concentration was about 18,000 mg/l). Larger concentrations of DBA allowed the use of fewer than normal operating pumps. The operation of the FGD system was extremely flexible, with three ways of improving SO_2 removal efficiency - DBA, additional pumps, and slurry pH.

TABLE 1. SECI SO_2 REMOVAL EFFICIENCIES WITH DBA ADDITION

Pumps in Operation	DBA (ppm)	SO_2 Removal Efficiency % *
4	135	84.8
4	270	88.5
4	300	90.11
3	550	86.7
3	1050	89.1
3	1100	89.2
3	1200	90.7
3	1250	90.4
3	1300	92.2
2	1500	85.7
2	1700	86.2

* at boiler loads greater than 600 MW

Economics of DBA Addition

With three available options for obtaining SO_2 removal efficiencies, an economic analysis was performed to determine the optimum combination of number of pumps operating and the DBA concentration required to meet SO_2 efficiency requirements.

Since SECI typically has wide load fluctuations, an FGD mathematical model was developed for the economic analysis, allowing prediction of SO_2 removal efficiencies as a function of load, DBA concentration, Cl^- concentration, and number of operating pumps. The model calculated power consumption, DBA cost, and estimated the rolling average of SO_2 removal efficiency, all integrated over the projected load demand for two out-years (provided by SECI).

In the analysis, fan power was ignored. The centrifugal fan has a control damper and, at constant volume, a decrease in FGD pressure drop (from turning off a pump) results in the corresponding increase in control damper pressure drop and relatively constant power consumption. DBA costs were known at $0.23/dry pound, however, a long term contract with a DBA vendor would certainly provide lower costs. Long term costs were estimated at from $0.15 to $0.21/dry pound and a DBA degradation rate of 4 times theoretical was assumed regardless of load for the operating cost analysis. Chlorides were assumed to be a constant of 22,000 mg/l based on material balance calculations of SECI provided coal analyses. Power costs were varied using SECI provided and approximated actual cost of avoided power rather than a cost of power that included annualized cost of the complete installation.

Additional assumptions were made to complete the model:

(1) Assume a 4% coal cleaning credit,

(2) Never fall below an instantaneous SO_2 removal efficiency of 84%,

(3) Maintain a rolling average of 86%,

(4) Drop to 3 modules at less than 400 MW, 2 modules at less than 220 MW,

(5) When high SO_2 removal efficiencies allow a pump to be dropped, a transition period was included (of 1/2 pump) to account for periods of time when load swings and uncertainty would prevent dropping a pump,

(6) Operation of two recycle pumps per module is the minimum.

Table 2 gives a representative summary of the calculated SO_2 removal efficiencies for one month with the use of DBA. Not shown is a similar analysis for operation without DBA. In all, 24 months were used to accurately calculate the operating costs with and without DBA. Yearly operating cost comparisons were made for operation with and without DBA and with varied DBA and power costs.

The results of this analysis indicate the amount of DBA required to avoid one pump per module is about 600 ppm. Thus, 600 ppm of DBA would allow operating the modules with three instead of four pumps. Due to the low cost of avoided power at SECI, it is more economical to operate with a low DBA concentration and more pumps. This is partly due to the safety limitation of scrubber operation with less than 2 pumps, which would be technically possible at high DBA concentrations and low loads.

TABLE 2. SUMMARY OF MODULE AND PUMP OPERATION FOR VARIOUS LOADS AT CONSTANT DBA CONCENTRATION.

% of Month at this load	Load MW	No. Modules	No. Pumps	SO_2 Removal Efficiency
8.74	620	4	3.0	84.10
2.42	589	4	3.0	85.07
1.47	558	4	3.0	86.17
1.35	527	4	3.0	87.18
1.48	496	4	3.0	88.22
1.34	465	4	3.0	89.28
2.82	434	4	2.5	87.09
5.78	403	3	3.0	86.48
9.95	372	3	3.0	88.02
14.38	341	3	2.5	86.72
17.88	310	3	2.0	83.75
10.75	279	3	2.0	85.84
6.45	248	3	2.0	88.02
7.66	217	2	2.5	86.56
100.00			Avg. =	88.70

After completion of the DBA test program and economic study, a permanent DBA injection system was designed and installed at both units of SECI. The system incorporates a metering pump which adds DBA to the mist eliminator wash tank as a linear function of load, and a spiking pump, capable of injecting large quantities of DBA to an individual module.

SODIUM THIOSULFATE - SCALE CONTROL THROUGH OXIDATION INHIBITION

In order to reduce mist eliminator scaling, a continuous supply of unsaturated wash water is required. Two methods of obtaining this water were devised for SECI:

1) Repipe the entire FGD system so that all fresh water makeup enters the system only at the mist eliminator section and at a constant rate, not the sawtooth makeup experienced with the use of the emergency pond system as a liquid capacitance.

2) Add sodium thiosulfate, an oxidation inhibitor.

Pilot plant tests (7) had indicated that less sodium thiosulfate is required when high Cl^- concentrations are present. The additive had been tested at Shawnee (5), where unsaturated operation was demonstrated. Other benefits of sodium thiosulfate considered were the improvement of crystal habit, and thereby better dewatering, and the potential for reduction in DBA consumption by elimination of oxidative degradation of the organic acids. On the negative side, the improved dewatering properties would reduce liquid blowdown, and thereby increase the Cl^- concentration. Increased Cl^- concentrations require higher DBA concentrations and increased dissolved calcium increases the DBA loss through coprecipitation in the calcium sulfite crystal.

SECI agreed to a short-term test of sodium thiosulfate. Initially, enough sodium thiosulfate was added to the system to provide a concentration of approximately 500-800 mg/l. Process liquor samples were taken every 24 hours from the absorber modules for gypsum saturation analysis. The results, presented in Table 3, show the dramatic decrease in gypsum saturation levels

TABLE 3. GYPSUM SATURATION LEVELS AT SECI AS A FUNCTION OF SODIUM THIOSULFATE CONCENTRATION.

Thiosulfate Concentration mg/l	Cl^- Concentration mg/l	Gypsum Saturation %
0	18900	151.02
0	18900	232.18
784	24900	14.69
538	24100	17.18
739	25300	6.08
560	28000	6.69
784	26000	4.78
536	23300	5.62
219	24300	10.19
233	25300	7.27
291	26200	5.63
335	25700	6.61
189	25000	22.03
364	27800	22.48

from 153 percent before addition of sodium thiosulfate, to 10-30 percent after addition. In addition, since the scrubbing liquid was unsaturated, existing gypsum scale dissolved into solution, and the previous areas of heavy gypsum scale were clean in a matter of days.

Since it is a strong possibility that sodium thiosulfate may pay for itself in reduced DBA losses, a test is scheduled to determine changes in DBA consumption when used in combination with sodium thiosulfate.

Cake moisture also improved from 50 percent solids before sodium thiosulfate addition, to 80 percent solids after addition. However, the Cl^- concentration remained relatively constant due to the need for supernate in the pugmill for the fixation process. Without the supernate, the filter cake, flyash, and lime mixture has insufficient moisture for the hydration reaction.

CLASSIFIED PRODUCT REMOVAL - IMPROVING CAKE PROPERTIES

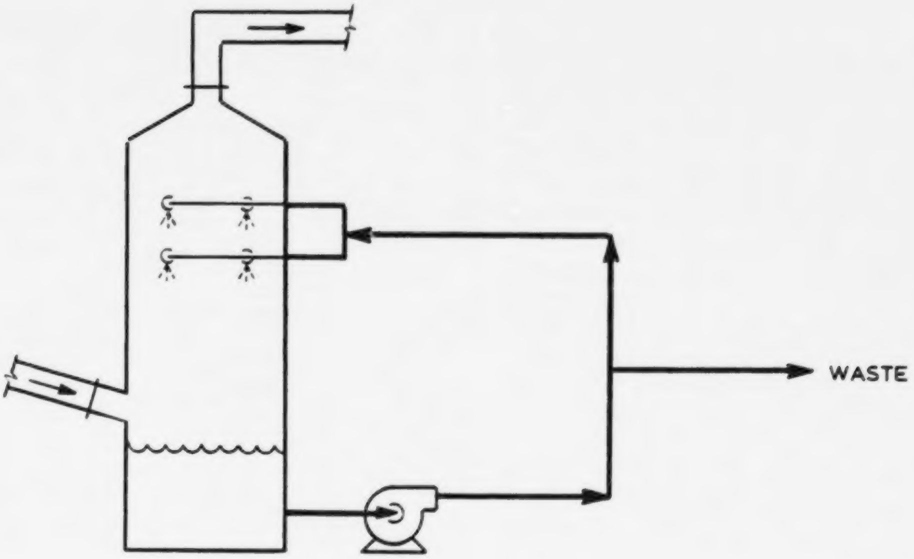
SECI's Unit 1 FGD system incorporates a unique classified product removal, or double draw-off (DDO), system which has resulted in improved product dewatering and substantially increased crystal size. The Unit 1 FGD system also incorporates a two-tank, in-situ, forced oxidation system.

DDO is a configuration of the standard FGD recycle tank which allows accelerated removal of fine particles. At SECI, a hydroclone is used to selectively dispose of fine particles, while a second stream allows removal of the product. This concept reduces total crystal surface area in the recycle tank, and crystallization takes place, primarily on the remaining, large crystals. Primary and secondary nucleation insure the continual production of new fines, so continuous, selective removal is always necessary.

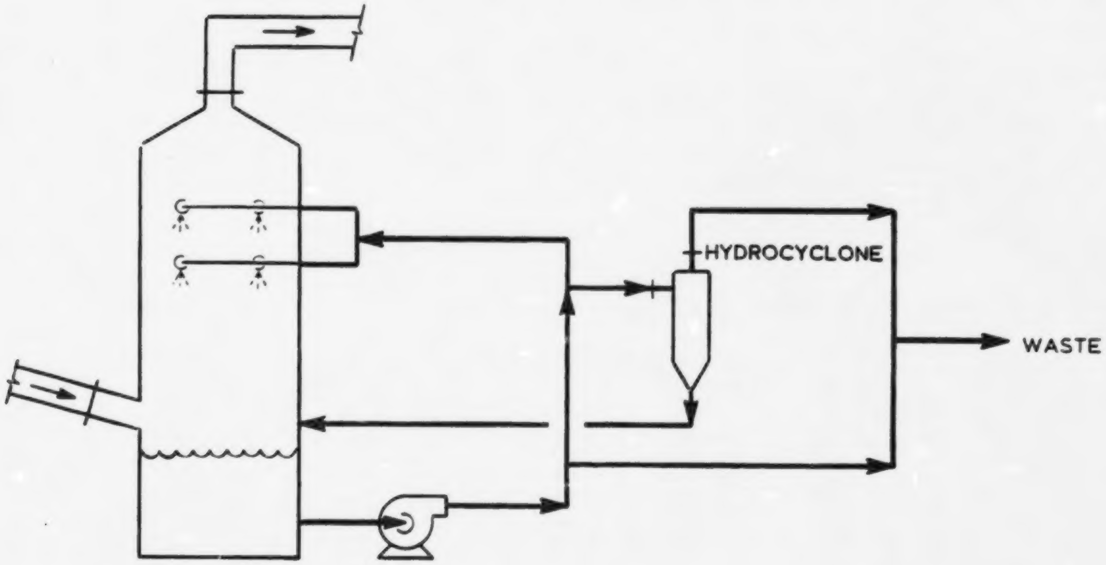
The DDO method also has the added benefit of producing larger quantites of supernate for use in the absorber without affecting density control.

Figure 1 is a simplification of the process. As shown, in a standard FGD system, the waste, or product stream is removed directly from the mixed recycle tank. At SECI, two product streams are withdrawn, one directly from the recycle tank and one from the overflow of a hydroclone. The two streams are mixed and pumped to a thickener and the resulting product stream density is independent of the recycle tank density, thus allowing considerably more supernate to be returned.

The crystals produced at SECI using the DDO system are much larger than those produced in a typical FGD system, and considerably larger than those produced in a bleed stream oxidation system. Photomicrographs of gypsum crystals are given in Figure 2 for a typical FGD system, Figure 3 for a bleed stream oxidation system, and Figure 4 for the SECI DDO crystallizer. The particle size distributions for a forced oxidation pilot plant and the SECI DDO system are given in Table 4. Also given in Table 4 is a recent particle size distribution from a natural oxidation DDO run using sodium thiosulfate.



STANDARD FGD SPRAY TOWER


HYDROCYCLONE
WASTE

FGD SPRAY TOWER WITH DDO

FIGURE 1 COMPARISON OF DDO SPRAY TOWER TO STANDARD FGD SPRAY TOWER

Reproduced from
best available copy.

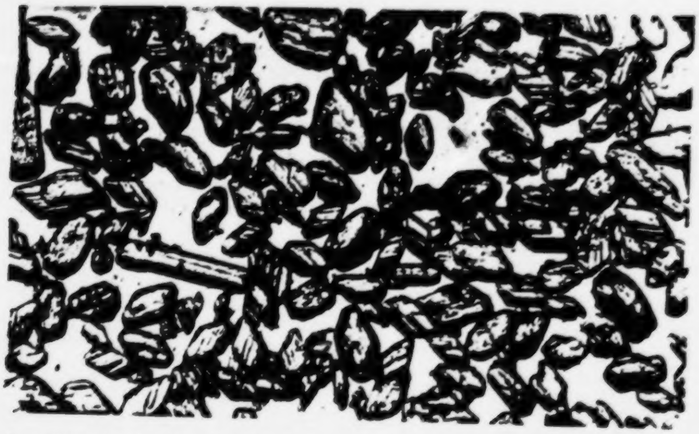


FIGURE 2 GYPSUM CRYSTALS - STANDARD FGD FORCED OXIDATION

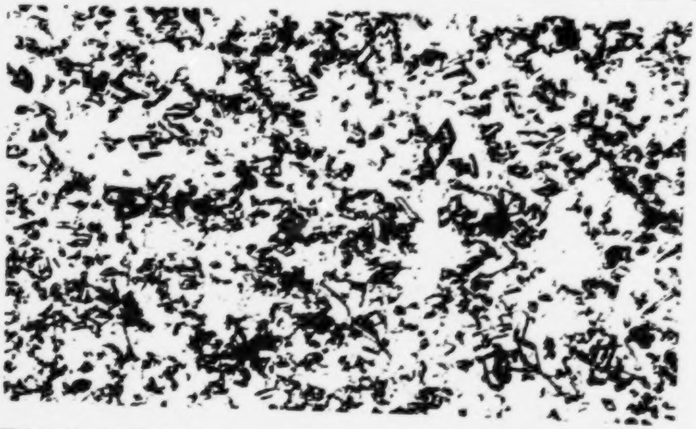
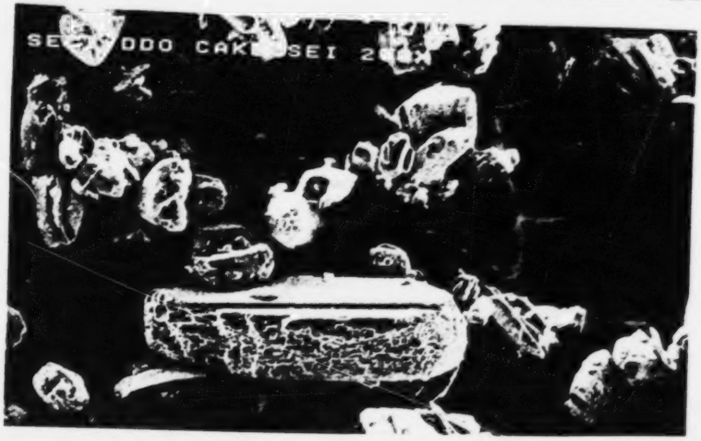


FIGURE 3 GYPSUM CRYSTALS - BLEED STREAM OXIDATION



FICURE 4 GYPSUM CRYSTALS WITH DDO AT SECI

Note the dramatic change in weight fraction of larger particles the DDO process provides in both the forced and natural oxidation mode of operation.

TABLE 4. PARTICLE SIZE DISTRIBUTIONS OF RECYCLE SLURRIES WITH AND WITHOUT DDO.

	Particle Size Microns	SECI Recycle Slurry Nat. Ox. & Thiosulfate with DDO Wt %	SECI Recycle Slurry Forced Ox. with DDO Wt %	Pilot Plant Recycle Slurry Forced Ox. without DDO Wt %
Greater than	45.0	35.01	53.08	0.68
	42.5	0.41	0.52	0.85
	36.0	0.72	1.30	16.19
	29.0	6.23	7.64	24.11
	22.8	7.40	10.74	21.25
	18.0	9.59	7.31	25.10
	13.0	10.46	10.83	5.11
	9.0	8.45	3.09	3.12
	6.5	3.13	3.57	1.62
	3.7	0.18	1.57	1.97
	1.2	0.27	0.35	0.20

The larger overall crystal size resulted in almost spectacular dewatering in the pilot plant drum filter. Cake thickness has been as much as two to three inches thick with some filtration rates over 800 lb/hr-ft^2. The resulting cake was easily molded (into a "snowball" for instance), and moisture could not be squeezed from the cake with hand pressure, as is typical of non-DDO cake. Table 5 gives preliminary results of filtration tests at SECI using a slipstream from the full scale unit and a pilot drum filter. Some chloride washing efficiencies were also obtained at very low wash displacements. As the pilot plant was designed for conventional cake filtration rates experienced in the past, when the very high filtration rates were encountered, there was insufficient wash water due to limitations in the wash water piping. The pilot program was temporarily suspended at the time of this writing due to equipment failure, but future tests will be performed at higher wash rates, and using other filtration devices such as a centrifuge and a belt filter, to produce cakes in excess of 90 percent solids. The DDO cake will also be tested as a substitute for natural gypsum in the production of wallboard.

TABLE 5. GYPSUM DEWATERING RESULTS ON A PILOT PLANT DRUM FILTER

Cl^- Conc. mg/l	Cl^- Washing Eff. %	Solids Conc. %	Filter Rate $lb/hr\text{-}ft^2$	No. Wash Displacements
22000	96.6	85.8	252	1.10
29000	57.7	84.8	587	0.40
30000	62.3	84.5	821	0.60
29000	97.8	83.2	454	1.00

SUMMARY

The combination of high chloride coal and truly closed-loop operation at SECI provided new and complicated areas of concern to reliable operation of an FGD system. The problems of closed-loop operation, including reduced SO_2 removal and plugging/scaling of the mist eliminators, were effectively solved using organic acid and sodium thiosulfate additives.

In addition, the first use of classified product removal has greatly enhanced the dewatering properties of the final cake.

ACKNOWLEDGEMENTS

The authors extend thanks to the following individuals, without whose support, this paper would not have been possible:

J. Duren	Seminole Electric Cooperative
J. Welborn	Seminole Electric Cooperative
M. Opalinski	Seminole Electric Cooperative
J. Pitman	Seminole Electric Cooperative
M. Swiger	Seminole Electric Cooperative

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

REFERENCES

1. Chang, J. and Laslo, D. Chloride effects on limestone FGD system performance. EPA/EPRI FGD Symposium, Hollywood, Florida, 1982.

2. Laslo, D. and Bakke, E. The effect of dissolved solids on limestone FGD scrubbing chemistry. Presented at the ASME 1983 Joint Power Generation Conference, Indianapolis, Indiana, September 27, 1983.

3. Laslo, D., Chang, J. and Mobley, J. Pilot plant tests on the effect of dissolved salts on lime/limestone FGD systems. EPA/EPRI FGD Symposium, New Orleans, Louisiana, 1983.

4. Chang, J. Pilot plant tests of chloride ion effects on wet FGD system performance. EPA-600/7-84-039, March, 1984.

5. Barkley, J. et al Sodium thiosulfate additive as an oxidation inhibitor in a limestone spray tower scrubber process. Presented at the 76th Annual Air Pollution Control Association Meeting and Exhibition, June 19-24, 1983, Atlanta, Georgia.

6. Rochelle, G., Owens, D., Chang, J., and Brna, T. Thiosulfate as an oxidation inhibitor in flue gas desulfurization processes: A review of R&D results. Presented at the Ninth EPA/EPRI Symposium on flue gas desulfurization. June 4, 1985.

7. Dempsey, J., Chang, J. and Mulholland, J. Operation of EPA owned pilot SO_2 scrubber and high temperature baghouse. Progress Report No. 7676-46, EPA Contract No. 68-02-3648, September, 1984.

8. Randolf, A. and Larson M. Theory of Particulate Processes, Academic Press, New York, 1971, p. 139.

9. Vaden, D. "Effects of Particle Size Classification on Gypsum Size Distribution in Simulated Stack Gas Scrubbing Liquors," M.S. Thesis, University of Arizona, December, 1981.

10. Midulla, R. and Peterson, J. Design and first year operational history of pollution control systems at Seminole Units 1 and 2. Presented at the American Power Conference, April 24-26, 1984, Chicago, Illinois.

11. PEDCo Environmental, Inc. Survey of design and actual chloride levels in commercial closed water loop FGD systems. Prepared for Peabody Process Systems, Inc., unpublished, February, 1982.

13. Burbank, D., and Wang, S. Adipic Acid Enhanced Lime and Limestone Testing at the EPA Alkali Scrubbing Facility - Final Report. PB-82-230-624, 1982.

14. Rochelle, G. Buffer Additives for Limestone Scrubbing - A Review of R&D Results. EPA/EPRI FGD Symposium, Hollywood, Florida, 1982.

15. Chang, J. and Mobley, J. Testing and Commercialization of Byproduct Dibasic Acids as Buffer Additives for Limestone FGD Systems. APCA Journal 33: 955, 1983.

16. Hicks, N.D., and Fraley, D.M. Commercial Application Experience with Organic Acid Addition at City Utilities of Springfield. Presented at the EPA/EPRI FGD Symposium Hollywood Florida (1982)

17. Ostroff, N. and Laslo, D. Use of Adipic Acid to Enhance Flue Gas Desulfurization, Presented at the 77th Annual Meeting of the Air Pollution Control Association, June 25, 1984, San Francisco, California.

DIBASIC ACID TEST AND CHEMICAL PROCESS EVALUATION AT PETERSBURG UNIT 3 FGD SYSTEM

by: D. Guetig
Indianapolis Power & Light Company
P.O. Box 436, Petersburg, IN 47567

S.Ou
Stone & Webster Engineering Corporation
P.O. Box 2325, Boston, MA 02107

C. P. Wedig
Stone & Webster Engineering Corporation
P.O. Box 2325, Boston, MA 02107

ABSTRACT

The use of dibasic acid (DBA) in a flue gas desulfurization (FGD) system buffers the scrubber chemistry, resulting in increased scrubber SO_2 removal efficiency. The use of DBA may also result in reduced scrubber electricity consumption. It is expected that Indianapolis Power & Light Company's (IPL) Petersburg Unit 3 can burn higher sulfur coal when using DBA in the scrubber, while maintaining its current 30-day average SO_2 control. However, long-term effects of factors that may limit scrubber performance (e.g., demister pluggage or dewatering equipment performance) have yet to be determined. Other effects of DBA addition, such as increased corrosion rates, also must be considered in long-term use of DBA.

The use of DBA at Petersburg Unit 3 did not reduce limestone consumption. The use of DBA on an annual basis or on an "as-needed basis" may result in increased scrubber reliability in that scrubber SO_2 emission excursions may be minimized. In addition, operation of the scrubber with DBA, lower booster fan inlet vane settings, and continued use of presently available coal should result in increased scrubber reliability because wet gas recirculation to the booster fans will be minimized.

PURPOSE AND SCOPE

The purpose of the process evaluation and the additive test program initially was to establish the FGD system baseline conditions and then determine the effect of a buffer additive on improving SO_2 removal and system reliability, and reducing demister scale formation. A major goal of the process evaluation also was to determine the limestone quality, grind, and slurry concentration.

Specific reasons for the additive tests are as follows:

- Determine percent sulfur coal that can be burned without exceeding allowable emissions
- Document FGD system process data
- Optimize limestone grinding circuit
- Evaluate use of buffer additive agent

The quantitative results were measured by changes in SO_2 removal, limestone consumption, waste characteristics, operating costs, demister section solids accumulation, and other parameters.

The Stone & Webster Engineering Corporation (SWEC) project included engineering, design, procedures, scheduling, purchasing, delivery, inspection, observation, checkout, training, sampling, testing, monitoring, analytical activities, evaluation, data reduction, and report preparation.

DESCRIPTION OF SWEC/IPL LABORATORY

The chemical analyses of samples collected during the entire test period (June 11 to August 24, 1984) were performed by various companies under the direction of SWEC. A description of these various laboratory facilities is as follows:

DBA TEST AND PROCESS EVALUATION EQUIPMENT

SWEC arrived onsite at Petersburg Unit 3 for an internal inspection on May 5, 1984, and set up a scrubber laboratory trailer.

This laboratory equipment, used during the entire test program, became the property of IPL when SWEC left the site on August 25, 1984.

COMMERCIAL TESTING COMPANY LABORATORY

SWEC employed Commercial Testing & Engineering Company (CTE) of Henderson, Kentucky, to perform some chemical analyses. The FGD samples were sealed in plastic bottles or bags and picked up by CTE.

IPL COAL LABORATORY

IPL operated a coal laboratory at the Petersburg Generating Station. IPL collected coal samples at each of the operating pulverizer outlets of Unit 3 and analyzed for sulfur using a LECO sulfur determinator. This sulfur information was given to SWEC for use during the test program. In addition, IPL prepared a composite coal sample (from all operating pulverizer outlets) which was given to SWEC for moisture, sulfur, and/or ultimate analyses.

MONSANTO CHEMICAL COMPANY

IPL employed Monsanto Chemical Company to perform DBA test on analysis work at their analytical laboratory, located in Gonzales, Florida.

ACUREX CORPORATION

SWEC employed Acurex Corporation to provide DBA chemistry consultation (Dr. J. Chang) and scrubber inlet flue gas testing. Acurex provided input into the chemistry of DBA and provided flue gas sampling and reports.

INDUSTRIAL CONTRACTORS

IPL employed Industrial Contractors to field assemble the DBA test equipment. SWEC provided equipment field checkout, startup, and personnel training.

LOG OF SAMPLES TAKEN DURING ENTIRE TEST PERIOD

SWEC took over 1000 samples while onsite during May 5 to August 24, 1984. Each sample was entered into a log of samples.

BUFFER ADDITIVE STORAGE AND INJECTION SYSTEM

SWEC and IPL designed and operated the temporary buffer agent additive delivery, storage, and injection system. The buffer agent additive tests were performed July 23 to August 24, 1984, using a Monsanto DBA mixture as the buffer agent additive. The DBA mixture is a water solution of adipic, glutaric, and succinic acids, which also contains a small amount of nitric acid. This mixture was delivered, stored, and added to the Petersburg Unit 3 FGD system as a 25 percent DBA by weight solution.

DBA DELIVERY

Twenty-five percent DBA solution at approximately 110°F was delivered to the Petersburg site from the Monsanto adipic acid manufacturing facility in Pensacola, Florida. Deliveries were made by McKenzie Trucklines in 40 ft x 8 ft x 12 ft, 5,000 gal, insulated stainless steel trailers which were backed into the unloading area in the vicinity of the electrical building opposite Module B. The McKenzie trailers used for transporting DBA had bottom unloading ports equipped with double shutoff valves and 3-inch quick-connect fittings. Each trailer arrived onsite with sufficient hose, fitted with 3-inch quick-connect fittings, so that the DBA could be unloaded into the storage trailer through the hatch located midpoint in the storage trailer top. Each delivery trailer tractor was equipped with its own self-contained transfer system, with an unloading capability of approximately 100 gpm.

DBA STORAGE

The trailer contents were transferred by self-contained equipment into the 6,700 gal insulated stainless steel. Storage trailer located in the vicinity of Module A, which was in close proximity to the IPL laboratory trailer and the buffer agent additive injection pump. The trailer was equipped with a standard manway, which facilitated access to the top of the trailer. In order to ensure that an adequate inventory of DBA was maintained throughout the test, the deliveries were closely coordinated with the test operation. The trailer discharge port (equipped with emergency hydraulic shutoff valve, a manual shutoff valve, and a 3-inch quick-connect male connection) was connected to the start of the hard-piped injection pump suction system (equipped with female connection) by a hose with 3-inch quick-connect fittings. Recirculated solution from the DBA injection system was returned to the storage trailer through the hatch located on top of the trailer.

TEMPORARY DBA INJECTION SYSTEM

The temporary DBA injection system consisted of a Gould injection pump, a pump suction piping system, a pump discharge and distribution piping system and a recirculation system, which returned the major portion of the pump discharge liquor to the storage trailer. All wetted surfaces in this system were either 316 or 316L stainless steel or materials having comparable corrosion resistance. The pump suction system consisted of:

- A 3-inch quick-connect female fitting to accept the 3-inch quick-connect male fitting attached to the storage trailer discharge hose
- A 3-inch to 1 1/2-inch reducer
- The following 1 1/2-inch size items: in-line strainer, shutoff gate valve, bimetallic thermometer with fitting, water flush system, and necessary pipe and fittings

Discharge from the Gould centrifugal injection pump was either pumped to the FGD system or recirculated to the storage trailer through 1-inch pipe. Under test design conditions, 25 percent (by weight) concentration DBA solution was added to the FGD system to maintain the DBA concentration. The remaining 85 to 90 gpm of liquor was returned to the storage tank. Control of the two streams was maintained by globe valves located in the recirculation line and in the FGD system feedline. The two valves were located in close proximity to the pump, to each other, and to the Badger oscillating piston totalizer meter located in the FGD system feedline.

The DBA solution was distributed to the four modules through individual rotameters and module downcomer injection ports. Bypass capability with the necessary valves was provided around each rotameter to permit servicing of the rotameters and addition of DBA, on a slugging basis, to each module. Slugging was necessary when large increases in FGD system DBA concentration were required, e.g., increasing the DBA concentration from 500 ppm to 1,000 ppm prior to the 1,000 ppm test period. Water flush capability for the recirculation, FGD system feed, and distribution systems was provided.

OPERATING AND MAINTENANCE PROCEDURE WITH DBA

There were two modes of test operations, 1) the constant addition of a relatively small amount of DBA to the FGD system using individual module rotameters and 2) the slugging of a larger amount of DBA to individual modules to provide gross increase in FGD system DBA treatment levels. For the addition of larger quantities of DBA, the rotameter(s) were bypassed and the addition amount was measured by the totalizer.

The flow of DBA to the individual modules required adjustments based on actual analyses of FGD system DBA concentration levels.

DBA crystal formation in the 25 percent DBA solution did not occur because the solution temperature did not drop below 70°F. Recirculation of the bulk of the liquor into the storage tank and the relatively quick turnover maintained pump discharge temperatures in excess of 110°F (e.g. 110°F to 140°F). DBA temperature levels in the individual module injection systems were checked at the rotameter calibration lines. The individual injection systems were flushed with water into the FGD system modules.

Maintenance procedures were as prescribed in the Gould, Badger, and Wallace and Tiernan instruction brochure provided with the totalizer, pump, and rotameters, respectively.

SWEC, Monsanto, and IPL trained over 30 IPL personnel in the safe O&M and safety considerations of the DBA system and laboratory procedures.

BUFFERING AGENT ADDITIVE TEST PROGRAM

SWEC performed buffering agent additive tests, along with specific sampling, monitoring, and analytical work, from July 23 to August 24, 1984. During this time period, both normal sulfur and high sulfur coals were burned. The tests were performed as follows:

- During the week of July 23, 1984, SWEC tested approximately 500 ppm buffering agent additive concentration in the absorber recycle tank, at a pH of approximately 5.7 to 5.8, to determine the effect of a moderate concentration of buffer agent at a moderate pH.

- During the week of July 30, 1984, SWEC tested approximately 1000 ppm buffering agent additive concentration in the absorber recycle tank, at a pH of approximately 5.7 to 5.8, to determine the effect of increased buffer agent additive at a constant pH.

- During the week of August 16, 1984, SWEC tested approximately 500 ppm buffering agent additive concentration in the absorber recycle tank, at a pH of approximately 5.2 to 5.3, to determine the effect of a moderate concentration of buffer agent at a low pH.

- During the last weeks of testing, August 13 and August 20, 1984, SWEC maintained approximately 1000 ppm DBA, at a pH of approximately 5.8 (the optimum buffering agent additive concentration and pH as determined by previous testing), to obtain long-term test results.

- During the last two days of testing, SWEC increased the DBA concentration to approximately 2000 ppm, at a pH of approximately 5.8, to document the effects of high DBA concentration on SO_2 removal.

Detailed written test and analytical procedures were adhered to during the test period. Appendix I presents the procedures for DBA concentration by titration. Figure 1 shows typical titration curves for deionized water, and filtered recycle tank slurry with and without DBA.

BUFFERING AGENT ADDITIVE TEST RESULTS

This section presents a summary of scrubber performance data collected during the DBA test period. The following is a description of the parameters:

- Unit 3 Load-MW gross was taken from the computerized Daily Summary for that day.

- Sulfur in coal was presented from composite samples of the mills in service and sent to Commercial Testing & Engineering (CTE). Percent sulfur basis was as sampled from mills.

- Booster fan inlet vane settings were actual board readings taken by SWEC.

- SO_2-stack monitor (ppmv wet) were taken from the stack monitor recorder.

- Adipic acid equivalent concentration was ppm by weight.

- Solids in slurry-recycle tank readings were taken by hydrometer or percent solids analyses.

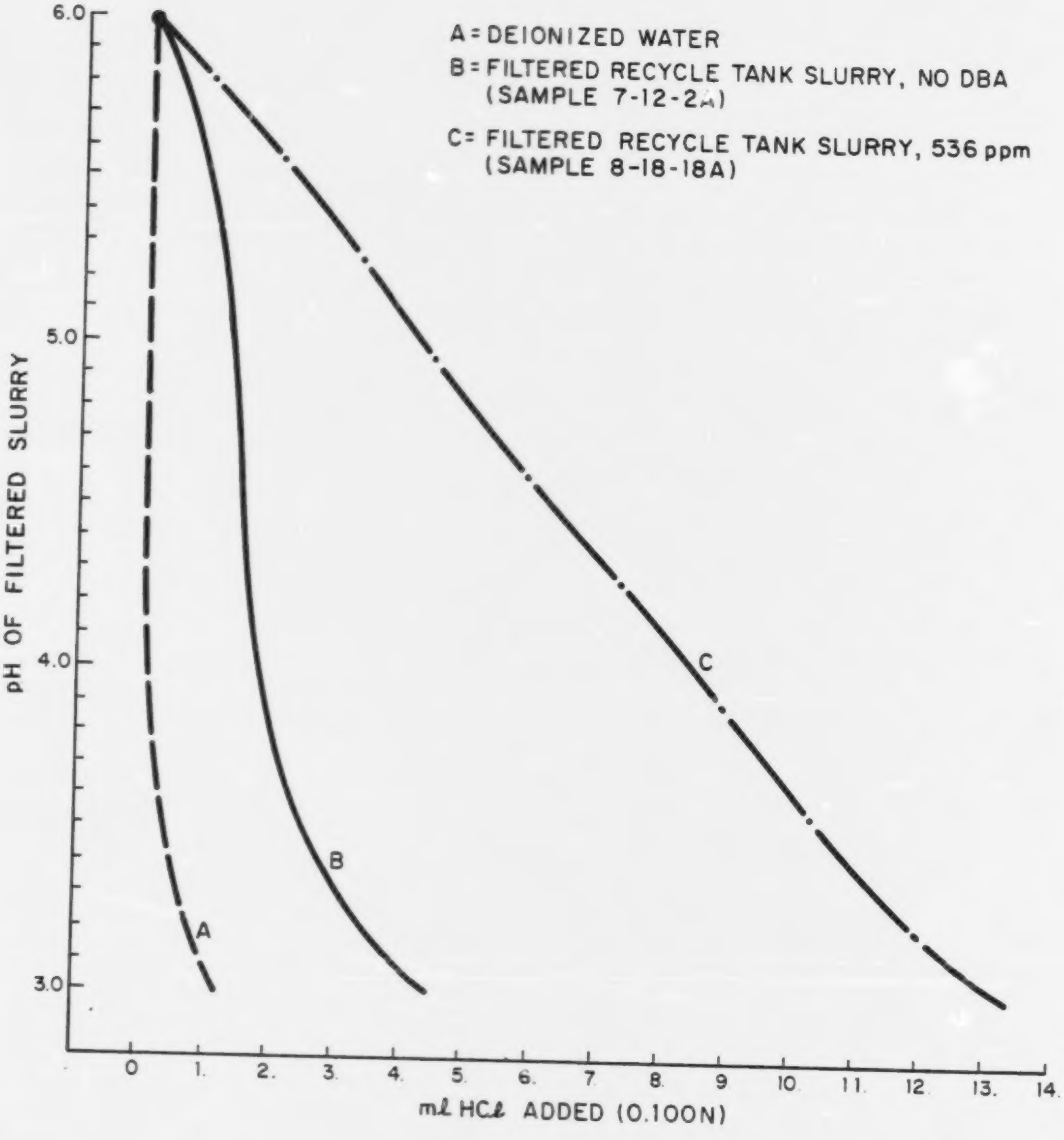


FIGURE 1
TITRATION CURVE FOR RECYCLE TANK SLURRY
WITH AND WITHOUT DBA

- Lb $SO_2/10^6$Btu, FGD system in/out: Inlet value was based on fuel sulfur analysis and calculation of HHV by Dulong equation (from coal ultimate analysis). Stack 3-hour averaged values were determined by using IPL equation and the SO_2 and CO_2 3-hour averaged values from the computerized daily emission logs.

- Module SO_2 removal was based on KVB monitor scrubber inlet/outlet readings. Modules A and B efficiencies were based on booster fan BFF-3-1 outlet duct readings, and Modules C and D efficiencies were based on BFF-3-2 outlet duct readings (inlet to scrubber).

- Stoichiometry (defined as Moles $CaCO_3$ added to scrubber per mole of SO_2 removed) was calculated from chemical analysis of Recycle Tank B slurry. Filter cake analyses were also used to estimate stoichiometry, but these were delayed by the residence time in the thickener.

- Sulfite-to-sulfate ratios were calculated from chemical analyses of Recycle Tank B and filter cake samples. Recycle tank slurry was used for this information.

- Limestone purity was obtained by chemical analyses.

CONSUMPTION OF DBA

Table 1 presents a summary of the DBA shipments received July 19 to August 23, 1984, at Petersburg Unit 3. During the SWEC DBA test period, the total amount of DBA used was approximately 75,000 lb (on a dry weight basis). The daily average gross generation during this period was 9,590 MWh, and the daily average SO_2 removed by the entire FGD system was 169 tons. The daily average DBA concentration in the scrubber modules was 730 ppm by weight adipic acid equivalent. Therefore, during the SWEC DBA test period, the consumption of DBA on a dry weight basis was as follows: 2,310 lb DBA/day, 0.24 lb DBA/MWh, and 13.6 lb DBA/ton SO_2 removed by the FGD system.

The usage of DBA at Petersburg, from August 13 to August 16, 1984, was determined. During this four-day period, the total amount of DBA solution used was approximately 5,200 gal, which is equivalent to 11,060 lb of DBA on a dry weight basis. The daily average gross generation was 10,360 MWh and the daily average SO_2 removed by the entire FGD system was 226 tons. As presented in Table 2, the daily average DBA concentration in the scrubber modules was 960 ppm by weight adipic acid equivalent. Therefore, during this high sulfur coal (approximately 3 percent sulfur) and 1,000 ppm DBA test period, the consumption of DBA on a dry weight basis was as follows: 2,760 lb DBA/day, 0.27 lb DBA/MWh, and 12.2 lb DBA/ton SO_2 removed by the FGD system.

TABLE 1. SHIPMENTS OF DBA (JULY 19 TO AUGUST 23, 1984)

	Shipment/Lot Number							
	1	1a*	2	3	4	5	6	7
Date Shipped	7/17		7/23	7/29	8/5	8/13	8/19	8/22
Date Received	7/19		7/25	7/30	8/6	8/14	8/20	8/23
DBA content, total wt,%	25.74	25.88	25.25	25.70	25.54	25.51	24.98	25.27
Adipic acid wt%	3.70	3.63	3.77	3.93	3.91	4.69	3.96	3.79
Glutaric acid,wt%	16.66	16.84	16.39	16.55	16.62	15.82	16.02	16.29
Succinic acid,wt%	5.38	5.41	5.09	5.81	5.01	5.00	5.00	5.19
Nitric acid,wt%	0.46	-	0.18	0.41	0.20	0.38	0.39	0.65
lb solution shipped	43,600	-	41,980	42,640	41,680	41,960	38,420	46,000
lb DBA (dry)	11,223	-	10,600	10,958	10,645	10,704	9,597	11,624
Butyric,ppm	11							
Valeric,ppm	20†							
Caproic,ppm	9							
Hydroxy Caproic,ppm	<50							
Boric Acid,ppm		12						
Vanadium,ppm	100.78	105.6						
Copper,ppm	2.89	5.6						
Mn,ppm		0.2						

NOTES:

*Sample removed from storage trailer and analyzed. Sample 7-23-20M taken 16:00 hrs on 7/23/84.

†Valeric acid is reported to be responsible for the bad odor of DBA.

TABLE 2. SO_2 REMOVAL EFFICIENCY ENHANCEMENT

Date	Time	MW	BFF % Setting 3-1,3-2	Coal %S and #SO_2/10^6	Average Module Efficiency and Range	FGD System Efficiency	Apidic ppm (All Recycle Tanks)	Control Board pH Recycle Tank	Total Pumps	Notes
	1030			2.84,4.69						
7-19	1400	527	100,100	2.84,4.71	86.6(82.5-91.5)	76.2	0	5.9-6.5	12	Baseline
	1500	534	100,100	2.84,4.71	86.7(81.5-92.6)	76.7	0	5.9-6.5	12	
	1600	524	100,100	2.84,4.71	86.9(80.6-92.9)	75.5	0	6.1-6.5	12	
	1700	530	100,100	2.84,4.71	89.2(83.3-93.1)	76.4	0	6.1-6.5	12	
	1800	523	100,100	2.84,4.71	89.6(87.5-92.9)	77.2	0	6.1-6.5	12	
	1900	530	100,100	2.84,4.71	84.2(75.9-91.3)	75.9	0	6.0-6.5	12	
	2000	528	73,78	2.84,4.71	86.6(82.1-89.4)	76.4	0	6.0-6.5	12	
7-23	0830	535	85,85	2.70,4.71	77.0(75.5-80.7)	74.0	0	6.0-6.2	8	
	0930	530	85,85	2.70,4.71	73.4(67.9-82.4)	72.5	0	6.0-6.1	8	
	1030	532	85,85	2.70,4.47	76.2(72.0-82.1)	73.2	0	6.0	8	
	1130	532	85,85	2.70,4.47	88.9(79.2-94.2)	75.3	Start	5.8-6.0	8	
	1230	530	85,85	2.70,4.47	94.0(92.3-95.8)	80.9	add DBA	5.9-6.0	8	
	1330	530	85,85	2.70,4.47	92.5(88.0-94.8)	82.0	500-650	6.0-6.1	8	500 ppm
	1430	530	85,85	2.78,4.56	92.9(87.2-95.4)	82.3	500-650	6.0-6.1	8	
	1530	535	85,85	2.78,4.56	91.4(86.4-95.0)	85.8	500-680	6.0	8	
	1630	537	85,85	2.78,4.56	93.0(88.5-94.9)	85.8	520-700	6.0	8	
	1730	524	85,85	2.78,4.56	92.9(88.6-94.7)	83.0	520-720	6.0-6.2	8	
	1830	529	85,85	2.78,4.56	90.7(85.8-94.4)	86.5	530-740	6.0-6.1	8	
	1930	533	85,85	2.78,4.56	90.2(85.0-94.7)	86.8	530-780	5.9-6.0	8	
7-24	0830	530	85,85	2.15,4.56	88.0(75.9-92.5)	80.2	200-820	5.8-6.1	8	500 ppm
	1030	523	85,85	2.15,3.58	84.6(76.4-87.8)	79.3	200-800	5.8-6.2	8	
	1200	510	85,85	2.15,3.58	84.2(73.7-88.9)	78.0	250-760	5.8-6.1	8	
	1330	524	85,85	2.15,3.58	82.3(76.5-91.4)	72.4	270-760	5.7-5.8	8	
	1440	526	90,90	2.15,3.58	86.4(77.8-91.1)	75.1	270-750	5.8	8	
	1450	524	80,80	2.15,3.58	85.8(77.4-91.7)	76.1	290-750	5.8	8	

TABLE 2 (Cont)

Date	Time	MW	BFF % Setting 3-1,3-2	Coal %S and #$SO_2/10^6$	Average Module Efficiency and Range	FGD System Efficiency	Apidic ppm (All Recycle Tanks)	Control Board pH Recycle Tank	Total Pumps	Notes
7-24	1520	525	80,80	2.15,3.58	84.2(77.6-92.4)	75.1	300-740	5.8	8	
	1545	523	70,70	2.15,3.58	85.3(79.8-91.9)	74.3	310-740	5.8	8	
	1608	529	70,70	2.15,3.58	87.4(82.3-93.0)	75.4	320-720	5.8	8	
	1635	529	60,60	2.15,3.58	88.4(75.1-95.9)	72.4	320-720	5.8	8	
	1658	517	60,60	2.15,3.58	88.9(76.4-96.1)	71.0	320-720	5.8	8	
	1720	518	50,50	2.15,3.58	94.8(90.4-97.2)	72.1	320-720	5.8-5.9	8	
	1745	522	50,50	2.15,3.58	94.6(90.2-97.1)	67.0	320-720	5.8-5.9	8	
8-13	1000	500	85,85	2.70,3.58	89.5(84.4-94.6)	81.9	900-1000	5.8	8	1000 ppm
	1030	-		2.70,4.566						
	1330	505	70,70	2.70,4.566	92.4(87.1-99.1)	70.1	960-1000	5.8	6	3 modules
	1430			2.99,4.99						
8-14	1030			3.06,5.13						
	1300	520	88,88		93.3(88.7-97.5)	78.8	1050-1150	5.8	8	1000 ppm
	1430			3.19,5.32						
	1439	520	88,88		91.7(86.5-96.8)	80.4	1050-1140	5.8	8	
	1800	526	75,75		89.2(85.3-94.8)	79.7	1050-1140	5.8	8	
8-24	1000	530	60,70	2.61, --	96.8(96.0-98.1)	--	1800-2000	5.8-6.0	8	2000 ppm
	1312	532	60,70	2.61, --	95.0(93.6-96.8)	--	1500-1900	5.8	8	

UPPER DEMISTER SOLIDS ACCUMULATION

Upper demister solids accumulation and resulting plugging was a continuing problem. If not controlled, the pluggage would result in restricted gas flow through the absorber modules and inability to treat sufficient flue gas as originally designed.

To quantify scale accumulation under different test situations, 20 upper demister sections were numbered with plastic tags and weighed to estimate solids accumulation rates. Each reinforced fiberglass demister section was weighed a minimum of three times and the weights were averaged. The average solids accumulation rate without any treatment was 0.732 lb/day. With DBA in the recycle tanks (and DBA eventually in the demister wash water reclaimed from the thickener), the rate was 1.518 lb/day. These results were inconclusive for the following reasons:

- The location of a demister section in the absorber vessel affects accumulation of solids. Due to nonuniform gas flow, uneven distribution of demister wash water, and uneven pluggage of the lower demisters, some areas of the upper demister were clean and others were entirely plugged across the vanes in a single absorber vessel.
- Accumulation of solids occurred in two distinct mechanisms ways--hard crystalline scale and soft slurry solids--either or both of which may be present in different areas of the same module's upper demister or on the same demister section.
- Burning high sulfur fuel (resulting in higher velocities of gas in the modules) for various lengths of time for the three test segments will carry over different amounts of slurry to the upper demister.

Although it appears that the DBA was not particularly effective in preventing solids from accumulating on the upper demister sections, some conclusions may be drawn from the test results:

- With the same sulfur fuel, the improved SO_2 removal efficiency (when using DBA) of the absorber vessels will permit operation of the scrubber at lower gas velocities and less carryover of slurry and pluggage resulting from the carryover.
- The hard crystalline scale on the upper demisters is not likely to be reduced by lower gas velocities and may require modification of the demister wash system.
- Some method of directly washing the upper demister on-line (preferably on an intermittent basis to reduce reheat load) may help the removal of both hard and soft types of solids buildup.

LIMESTONE UTILIZATION

Limestone stoichiometric ratio values were determined before and during the DBA tests. During the baseline period of June 11 to July 22, 1984, the average limestone stoichiometric ratio was 1.19 in Recycle Tank B and 1.19 in the filter cake. During the DBA test period, the average limestone stoichiometric ratio was 1.18 in Recycle Tank B and 1.18 in the filter cake. No significant increase or decrease in stoichiometric ratio values can be attributed to the use of DBA. This observation is unique to the Petersburg Unit 3 FGD system in that many of the utilities that tested DBA found dramatic improvements in limestone utilization. The reason that use of DBA did not affect limestone utilization at Petersburg Unit 3 is that during the DBA test, the limestone was of high quality and fine grind.

SO_2 REMOVAL EFFICIENCY ENHANCEMENT

The addition of DBA clearly improved SO_2 removal efficiency in the absorber modules and therefore overall SO_2 removal efficiency of the FGD system. Table 2 summarizes some key data which demonstrate the improved SO_2 removal. Some module SO_2 removal efficiencies were as high as 97 percent (for example, on July 24, 1984 at about 500 ppm DBA); however, other modules were at 75 percent removal efficiency. This inherent variability among the modules was not predictable over periods of up to several days, although the average performance of the four absorber modules over a longer averaging time, e.g., 30 days, is expected to improve.

Some specific short-term results of particular interest are highlighted below:

- 0 to 500 ppm DBA. A difference was observed on the first day of DBA addition. The average module efficiency ranged from 68 to 82 percent before addition of DBA improved to a range of 85 to 96 percent after approximately 500 ppm adipic was slugged to the recycle tanks. This increase in SO_2 removal was observed within 10 to 20 minutes of slugging each of the recycle tanks. On July 23, 1984, Unit 3's boiler was kept at full load, booster fan vanes were kept at 85 percent, none of the spare recycle pumps were run, and pH was controlled to 6.0 (±.1). The coal sulfur content averaged 2.7 percent (as burned), ranging from 2.5 to 3.0 percent.

  An improvement can also be seen by comparing the operation of July 19, 1984, with 2.4 to 3.2 (average 2.8 percent as burned) sulfur fuel without DBA at high pH (greater than 6.0) and all spare recycle pumps running, versus later operation on July 23 1984, with DBA, pH = 6.0, and no spare recycle pumps in operation.

- 500 ppm DBA. At about 500 ppm adipic acid concentration the module efficiencies were in the 85 to 96 percent range at pH = 6.0 and of 74 to 97 percent range with pH = 5.8, with 85 percent booster fan vane settings. On July 24, 1984, the sulfur content of the coal averaged 2.2 percent (as burned), ranging from 2.0 to 2.4 percent.

- 1000 ppm DBA. At 1,000 ppm, the module efficiencies improved to about 90 percent (averaging from 84 to 99 percent) even at pH 5.8, still with no spare recycle pumps running. The sulfur content of the coal ranged from 2.3 to 3.4 percent, averaging 3 percent (as burned).

- 2000 ppm DBA. The scrubber was operated for one day with a DBA concentration of 2000 ppm. Based on very limited data at one operating point (pH = 5.8 and booster fan vanes set at 6.0 to 70 percent), it appears that the module efficiencies increase between 1 to 22 percent when compared to operation without DBA (pH over 6.0, booster fan vanes at 100 percent). The coal sulfur averaged 2.6 (as burned) percent on that day.

In Table 2, "FGD System Efficiency" is the overall efficiency of the scrubber, calculated from stack monitor data (lb $SO_2/10^6$ Btu) and inlet lb/10^6 Btu derived from fuel analyses.

Also in Table 2, "Recycle Tank pH" was taken from control board readings. The actual (SWEC measured) pH of the recycle tanks were 0.1 or 0.2 pH units lower than the control board readings since the procedure for determining recycle tank pH results in higher readings. The difference was less near pH = 6.0 and greater at pH = 5.6 or pH = 5.8.

EFFECTS ON THICKENER AND VACUUM FILTER PERFORMANCE

The operation of the thickener during the test was definitely affected, but not adversely changed by the short-term addition of DBA to the recycle tanks, even at a high (500 ppm) thickener overflow (reclaim water) concentration. It will be necessary in any long-term use of DBA to monitor the effects on dewatering equipment. In particular, inspection and evaluation should be made in the areas of 1) increased corrosion due to operation at lower pH, 2) possibility of filter cloth blinding, and 3) changes in pumping and polymer addition rates.

During the period of low sulfite-to-sulfate molar ratio (indicating higher oxidation of $CaSO_3$ to $CaSO_4$), there were occasional "spikes" of thickener underflow concentrations to 45 percent and above showing on the recorder in the FGD control room. The high solids concentration transients were very short and not verified by actual samples. The high thickener underflow concentration may result in loss of suction on the thickener underflow pumps or storage of the thickener rake

The pumps did not trip even after several "high" solids excursions, and the rake drive amperage was actually noticeably lower. The variation in sulfite-to-sulfate concentration did not cause an unacceptable mode of operation.

Another variation in thickener operation was observed in that the thickener underflow solids concentration would drop rapidly (instead of previously normal operation where it would decrease slowly) on pumping to the waste slurry tanks, sometimes from 30 percent to 10 percent in less than an hour. This can be attributed to variation in oxidation (i.e., lower sulfite-to-sulfate molar ratio) which appears not to be caused by DBA addition. The low solids concentration recovers rapidly also, on recirculation of slurry to the thickener feedwell. Since this is not an unrecoverable change (i.e., tripping the thickener rake or underflow pumps), it was not investigated further.

Vacuum filter performance appeared to be the same, although the vacuum filter cake solids increased slightly during DBA use. During the baseline period, the average solids content in the vacuum filter cake was 53.4 weight percent, whereas during the DBA test period of August 5 to August 14, 1984, the average solids content was 59.2 weight percent (solids include water of hydration). The improvement can be partly attributed to the lower sulfite-to-sulfate molar ratio which, again, appears to be caused by changes in pH rather than DBA addition.

One result of the DBA test is that the IUCS sludge stabilization system operated for a longer period of time than before the DBA test. This is caused, for the most part, by the higher sulfur fuel being used in the test period (more SO_2 was removed, consuming more limestone and producing more sludge).

Sometimes, both vacuum filters had to be operated at the same time (ordinarily one is sufficient to keep up with sludge production). The filter cake percent solids did not appear to be reduced or otherwise degraded by this mode of operation. The fly ash and lime feed systems appeared to be adequately sized to handle the increased requirements, and the pug mill was able to mix the higher solids loading. The filtrate pumps, however, were not capable of keeping up with the additional filtrate flow, and the floor of the IUCS building flooded under these high sulfur coal burn conditions.

DECOMPOSITION OF DBA

Tables 1 and 3 present the chemical analysis of samples containing DBA. As presented in Table 1, an analysis of a DBA solution sample (sample 7-23-20M of shipment No. 1) indicates no significant decomposition of the DBA in the storage after over four days of recirculation. This may be due to the very low nitric acid content of the Monsanto DBA. Very low nitric acid content is recommended for long-term operation of a buffer additive system. As presented in Table 3, the percentage of "other organic acids" did not significantly increase, indicating that the DBA may have decomposed to carbon dioxide and water.

Table 4 presents the dry weight percent of each of the DBA species (i.e., adipic, glutaric, and succinic) for the DBA storage tank, recycle

TABLE 3. CHEMICAL ANALYSIS OF SAMPLES CONTAINING DBA

Sample	Adip.(%)	Glut.(%)	Succ.(%)	Nitric as NO3(%)	Boric as B (%)	Ca(%)	Mg(%)	Mn(%)	Cl(%)	F(%)	Fe(%)	Cu(%)	V(%)	Other Organic Acids (%)
AGS Mixture (7-23-19M)	3.63	16.84	5.41	754	12	--	--	0.2	--	--	--	5.6	105.6	<1
Vac. Filter Filtrate 7/24	16	66	18	2.3	--	--	--	1.2	--	--	--	0.01	<0.1	<1
Recy. Tk. "C" Slurry 7/24	79	390	78	6.2	--	--	--	16.5	--	--	--	0.10	0.3	<1
Recy. Tk "B" Slurry 7/24	64	293	47	2.1	610	--	--	16.5	--	--	--	0.10	0.3	<1
Recy Tk. "B" 7/23	81	387	75	3.3	--	--	--	18.1	--	--	--	0.10	0.3	<1
Recy. Tk. "D" 7/26	92	319	4	0.1	434	--	--	--	--	--	--	--	--	<1
8/1/6M (RTB)	79	309	4	<0.1	496	--	--	1.8	--	--	--	0.20	<1	<1
8/17M (Reclaim)	42	238	4	<0.1	273	--	--	1.6	--	--	--	0.10	<1	<1
8/2/8M RTB	71	431	8	<0.1	537	--	--	3.9	--	--	--	0.10	<1	<1
8/6/8M RTB	130	505	6	<0.1	405	558	1600	--	--	--	--	0.05	--	<1
8/6/9M Reclaim	78	253	35	<0.1	312	684	1280	--	--	--	--	0.05	--	<1
8/8/9M RTB	86	242	ND	ND	485	356	2900	2.42	1219	21	15	--	--	<1
8/8/23M D-Duct	ND	ND	11	ND	19	162	467	68.00	15	1	2467	--	--	<1
8/13/14M RTB	134	426	7	1.9	673	467	4200	2.20	1472	23	0.76	--	--	<1
8/14/11M Reclaim	72	240	ND	ND	320	472	2267	1.44	767	18	0.22	--	--	<1
8/17/9M RTB	157	489	6	5.0	684	346	6733	1.65	1590	26	0.51	--	--	<1
8/22/7M RTA	69	530	69	ND	316	439	2933	2.98	825	19	1.21	--	--	<1
8/24/8M RTB	291	1015	210	4.9	496	401	2533	2.8[illegible]	1247	--	--	--	--	<1
8/24/11M Reclaim	120	298	31	ND	268	503	2867	1.96	674	--	--	--	--	<1

Note: All results in ppm by weight of the specie unless otherwise indicated.

TABLE 4. DRY WEIGHT PERCENT OF DBA SPECIES

Date	DBA In Storage Tank			Recycle Tank			Reclaim Water		
	Adipic	Glutaric	Succinic	Adipic	Glutaric	Succinic	Adipic	Glutaric	Succinic
7-23	14.0	65.1	20.9	14.9	71.3	13.8			
7-24	14.0	65.1	20.9	15.0	71.9	13.1	16	66	18
7-26	14.9	64.9	20.2	22.2	76.8	1.0			
8-1	15.5	64.4	20.1	20.2	78.8	1.0	14.8	83.8	1.4
8-2	15.5	64.4	20.1	13.9	84.5	1.6			
8-6	15.5	64.4	20.1	20.3	78.7	1.0	21.3	69.1	9.6
8-8	15.3	65.1	19.6	26.2	73.8	0			
8-13	15.3	65.1	19.6	23.6	75.2	1.2			
8-14	15.3	65.1	19.6				23.1	76.9	0
8-17	18.4	62.0	19.6	24.1	75.0	0.9			
8-22	15.9	64.1	20.0	10.3	79.3	10.3			
8-24	15.0	64.5	20.5	19.2	67.0	13.8	26.7	66.4	6.9
Average Weight Percent in Solid DBA	15.4	64.5	20.1	19.1	75.7	5.2	20.4	72.4	7.2

tanks, and reclaim water. The data on this table indicate that succinic acid decomposes readily in the environment of the scrubber module (e.g., flue gas environment).

Table 5 presents the dry weight ratio of DBA species in the DBA storage tank, recycle tanks, and reclaim water. This table indicates that the decomposition rate of succinic acid is greater than adipic or glutaric acid and that the decomposition rate of glutaric is slightly greater than adipic acid.

EVALUATION OF DBA USE

The following is a summary of advantages and disadvantages of using DBA in the Petersburg Unit 3 FGD system.

Advantages:

- Short-term improvement in module SO_2 removal efficiency
- Possible higher reliability
- Possible reduction in demister pluggage (although this was not observed)
- Reduction of electrical power consumption

Disadvantages:

- High initial system cost and DBA cost
- No observed improvement in stoichiometric ratio (i.e., no reduction in limestone consumption)
- Possible detrimental effect on materials of construction (which could lower reliability)
- Possible acid safety concerns (although no safety problems occurred during the test)

PROCESS EVALUATION

SWEC performed a process evaluation of the Petersburg Unit 3 FGD system to determine the performance of the limestone grinding circuit and obtain FGD system baseline data. The baseline data allowed SWEC to compare the performance of the FGD system with and without the effects of buffer agent additive. SWEC performed specific sampling, monitoring, and analytical work during this evaluation.

TABLE 5. WEIGHT RATIO OF DBA SPECIES IN SAMPLE

Date (1984)	DBA In Storage Tank		Recycle Tank		Reclaim Water	
	(Succinic/ Adipic)	(Glutaric/ Adipic)	(Succinic/ Adipic)	(Glutaric/ Adipic)	(Succinic/ Adipic)	(Glutaric/ Adipic)
7-23	1.49	4.64	0.926	4.78		
7-24	1.49	4.64	0.86	4.76	1.12	4.12
7-26	1.35	4.34	0.043	3.47		
8-1	1.30	4.17	0.051	3.91	0.095	5.67
8-2	1.30	4.17	0.113	6.07		
8-6	1.30	4.17	0.046	3.88	0.45	3.24
8-8	1.28	4.25	0	2.81		
8-13	1.28	4.25	0.052	3.18		
8-14	1.28	4.25			0	3.33
8-17	1.07	3.37	0.038	3.11		
8-22	1.26	4.05	1.0	7.68		
8-24	1.37	4.30	0.722	3.49	0.26	2.48
Average Weight Ratio	1.3	4.2	0.35	4.3	0.38	3.8

SO_2 REMOVAL WITHOUT DBA

Scrubber performance data were collected during the baseline period (July 16 to July 20, 1984). Of particular interest was the attempt on July 19, 1984, to burn high sulfur coal without DBA. Regulatory compliance was met during this test, but the scrubber had to be operated with very high booster fan inlet vane settings, spare recycle pumps, and high pH, resulting in a lower scrubber reliability.

LIMESTONE QUALITY

The limestone used by IPL during the period of June 11 to August 16, 1984, was of a very good quality. The total $CaCO_3$ ranged from 93 to 97 percent by dry weight, with an average of 95 percent $CaCO_3$. The $MgCO_3$ content of the limestone was very low, ranging from 0.35 to 2.6 percent $MgCO_3$ by dry weight, with an average of 1.2 percent $MgCO_3$.

The inerts (SiO_2, Al_2O_3, dirt, etc.) were as expected for a scrubber quality limestone, ranging from 3.2 to 5.3 percent inerts on a dry basis with an average of 3.8 percent inerts.

The moisture content of the limestone was found to be low, ranging from 0.1 to 2.2 percent by weight. This low moisture content was due to the hot summer environment of the limestone pile and the fact that it rarely rained during the test period.

The limestone reactivity test is a relative test that allows a utility to identify limestone which has nonreactive $CaCO_3$. The limestone reactivity values were good during the test period, the average value being 0.67. The limestone reactivity test was conducted as follows:

- A limestone, ground to pass through a No. 200 sieve and to be retained on a No. 325 sieve, was slurried in distilled water and reacted with a less than stoichiometric amount of hydrochloric acid.

- The acidity pH of the slurry was monitored.

- The time from acid addition to pH recovery to a value of 5.50 was determined.

The sooner the slurry pH reached the value of 5.5, the more reactive was the limestone. A response time of 15 minutes or less was set as the criterion for a stone to be used for FGD purposes. To determine if this criterion was met, the time required for the slurry pH to recover to pH = 5.50 was divided by 15.0 minutes. If the answer was less than 1.0, it was determined that the limestone may be useful for FGD purposes, but should be tested further by more elaborate test methods.

GRIND OF LIMESTONE SLURRY

The limestone slurry fed to the scrubber modules and passing a 325-mesh wet sieve ranged from 74 to 92 percent by weight, with the test period average being 87 percent.

Sieve analysis and particle size distribution data indicate that the ball mill ground the limestone, and the classifiers worked. For example, the order of fineness was as expected: limestone recirculation slurry, classifier overflow, transfer tank, classifier underflow, and ball mill discharge. A comparison of data indicated that the limestone fed to the scrubber was significantly more fine on August 16 than on July 19, 1984.

The particle size of the slurry fed to the limestone slurry storage tank was larger than the particle size of the slurry fed to the scrubber modules. This may have been due to the grinding caused by the pumps and agitator of the limestone slurry storage tank.

LIMESTONE SLURRY SOLIDS CONTENT

From June 13 to July 19, 1984, the average solids content of the limestone slurry that leaves the ball mill and enters the classifiers (ball mill discharge samples) was 52 percent by weight. The average solids content of the limestone slurry that leaves the bottom of the classifiers and returns to the ball mill (classifier underflow) was 58 percent by weight. During this same period, the average solids content of the limestone slurry that leaves the top of the classifier and enters the limestone slurry storage tank (classifier overflow) was 38 percent by weight. The classifiers were performing as expected in that the ratio of classifier underflow to overflow solids percent by weight content varied from 1.25 to 1.8. Based on the average (June 13 and July 10) information, approximately 72 percent of the total weight of slurry that entered the classifiers was returned to the ball mill as classfier underflow. This means that only 32 percent of the total slurry weight that enters the classifiers goes to the limestone slurry storage tank.

If the total limestone solids fed to the ball mill is assumed to be 16 tph, then the limestone solids fed to the limestone slurry storage tank would equal 16 tph, the limestone solids returned to the ball mill would equal 70.5 tph, and the limestone solids discharged from the ball mill (fed to the classifiers) would equal 86.5 tph. In this example, the limestone slurry storage tank receives 45.7 tph slurry, the classifiers are fed 163.2 tph from the ball mill, the classifiers return 117.5 tph slurry to the ball mill, the limestone silo feeds 16 tph limestone, and the makeup water to the ball mill is 29.7 tph. This means that the so-called "16 tph" ball mill actually "grinds" 163.2 tph of slurry.

The specific energy (horsepower hours per short ton of limestone fed at pinion shaft) for the Petersburg Unit 3 ball mill is approximately 31, assuming 100 amp ball mill motor at 90 percent efficiency and 16 tph limestone feed. This value of specific energy is similar to the KVS recommendation for a wet grinding closed-circuit, which produces a product size of 95 percent passing a 325-mesh sieve, with a 3/4 x 0-inch limestone fed at 10.0 kWh/ton limestone work index (1). The Petersburg Unit 3 limestone is usually 3/4 x 0 inch in the summer and 3/4 x 1/4 inch in the winter; the larger sizes are easier to move in freezing conditions. The limestone work index at Petersburg normally varies from 10 to 11.

The solids content of the limestone slurry fed to the scrubbers during the test period ranged from 20 to 36 percent by weight solids, with an average value of 29 percent by weight solids. This range and average percent solids content are considered relatively low when compared to other limestone FGD systems. Burning high sulfur coal resulted in very low solids content of the limestone slurry fed to the scrubbers. This was because water was added to the limestone slurry storage tank to prevent low level.

pH OF LIMESTONE SLURRY FED TO THE SCRUBBERS

The pH of limestone slurry in pure water is usually 9 to 10. The use of DBA lowered the pH of the limestone slurry to an average value of 7.4 in the limestone slurry storage tank from July 30 to August 21, 1985. This lower pH was due to the buffering action of the DBA found in the makeup water of the ball mill circuit (i.e., reclaim water).

FLUE GAS TESTING

Flue gas testing was conducted on July 25 and 26, 1984, by SWEC and Acurex to determine SO_2 levels and booster fan outlet flue gas flow rates and to conduct KVB monitor calibration checks.

SAMPLING AND ANALYTICAL PROCEDURES

Flue gas sampling was conducted in accordance with the U.S. Environmental Protection Agency (EPA) "Standards of Performance for New Stationary Sources," Methods 1 through 4, and 8 (2). A modified Method 8 was used for the SO_2 sampling.

Prior to and following the test runs, velocity traverses were conducted at each inlet gas duct location (3-1 and 3-2). Location 3-1 is the horizontal duct (south side) which is downstream of the common crossover duct and feeds flue gas to the Modules A and B inlets. Location 3-2 is the horizontal duct (north side) which is downstream of the common crossover duct and feeds flue gas to Modules C and D. Each rectangular duct was divided into 20 equal areas, and flue gas velocities and temperatures were measured at each midpoint in accordance with EPA Methods 1 and 2. Flue gas flow rates were calculated from the preliminary and post velocity traverse data. Flue gas moisture content was determined using the volumetric condensate procedure.

Triplicate 20-minute sampling runs were conducted. Flue gases were withdrawn for 20 minutes at a single sampling point.

Laboratory procedures for the determination of SO_2 in the hydrogen peroxide impinger solution were conducted as required in the Federal Register (3).

KVB MONITOR CALIBRATION PROCEDURES

Acurex supplied calibration gases of known SO_2 concentrations. Upon SWEC's signal, Acurex injected the calibration gases into the monitors.

The continuous KVB monitor sampling system sampled the known quantity of calibration gases at programmed intervals. The actual composition of the two bottles of calibration gas contained 407 ppm and 2195 ppm SO_2 by volume with the balance being nitrogen.

FLUE GAS TEST RESULTS

Concentrations are expressed in parts per million volume on a dry weight basis (ppmv (SO_2 (dry)). Concentrations at Location 3-1 ranged from 1,397 to 1,487 ppm and from 1,470 to 1,674 ppm SO_2 at the Location 3-2 inlet. The average of all flue gas test values was 1,513 ppm SO_2 as compared to 1,710 ppm SO_2 for the KVB monitor readings. The KVB monitor readings were consistently higher (averaging 13 percent higher) than the values obtained from flue gas testing.

The average of the Location 3-1 values was 1,450 ppm SO_2 and the average of the Location 3-2 values was 1,576 ppm SO_2. The Location 3-2 values were consistently lower (averaging 8 percent lower) than the Location 3-1 values.

The overall average dry volume composition of the flue gas tested was 1,513 ppm SO_2, 12.4 percent CO_2, 6 percent O_2, and 81.6 percent N_2. The overall average moisture content of the flue gas tested was 9.8 percent H_2O. The overall average molecular weight of the wet flue gas tested was 29.

During the flue gas testing, the booster fan inlet vane setting was 75 percent open for each fan, the average boiler load was 495 MW (net), the average temperature was 314°F, the average booster fan discharge pressure was 17.8 in. (H_2O), and the average amount of flue gas processed by each scrubber module was 570,000 acfm.

KVB MONITOR CALIBRATION RESULTS

A KVB six-point extractive flue gas SO_2 monitor (two inlet and four outlet points) was used as an operator tool to provide information for process adjustments. This was not the certified stack monitor. The KVB monitor was calibrated during July 25 to 26, 1984. Based on average readings, the KVB monitor was accurate within +2.1 percent for the 2000 ppm end and accurate within +12 percent for the 400 ppm end. The KVB monitor read consistently higher values than actual. Based on the results of this calibration period, SWEC and IPL deemed the KVB monitor accurate enough for use during the entire SWEC test period.

COAL ANALYSIS

This section of the paper presents the analysis of the coal burned during the process evaluation and DBA test periods of June 11 to August 15, 1984. The ultimate analysis and sulfur analysis were performed by Commercial Testing and Engineering Company for SWEC.

ULTIMATE ANALYSIS

The following Dulong equation was used to estimate the higher heating value (HHV) expressed in Btu/lb.

$$\text{HHV} = 14{,}544(C)+62{,}028(H-O/8)+4050(S)$$

where:

C = Carbon by weight fraction
H = Hydrogen by weight fraction
O = Oxygen by weight fraction
S = Sulfur by weight fraction

The HHV (expressed on a dry basis) of the coal burned during the test periods was very consistent, with a range of 12,631 to 12,935 Btu/lb and an average of 12,785 Btu/lb (on a dry basis). The ratio of chlorine to fluorine (on a weight basis) varied from 3.3 to 62, with an average of 20. The ratio of sulfur to chlorine (on a weight basis) varied from 9.5 to 243, with an average of 95.

Before the start of testing, IPL stockpiled approximately 120 hours of high sulfur coal (Arlen mines). This high sulfur coal was selectively burned during the DBA test period.

SULFUR CONTENT OF COAL

The sulfur content of the coal burned during the period of June 11, to August 23, 1984, was determined. The SO_2 release (lb SO_2 per million Btu) was estimated assuming no sulfur capture in the boiler or electrostatic precipitator and using the last previous Dulong-calculated HHV. The sulfur content varied from 1.92 to 3.66 percent by weight on a dry basis, with an average of 2.8 during the entire test period. The SO_2 into the FGD system varied from 2.97 to 5.78 lb SO_2 per million Btu, with an average of 4.36.

During the period of June 11 to July 11, 1984, the average SO_2 into the FGD system was 3.83 lb SO_2 per million Btu. During the baseline data collection period, the average SO_2 into the FGD system was 4.18 lb SO_2 per million Btu. During the DBA test period (July 23 to August 23, 1984), the average value was 4.6 lb $SO_2/10^6$ Btu to the FGD system.

DAILY AVERAGE PERFORMANCE

During the baseline test period of July 16 to July 22, 1984, the daily average gross generation was 9,980 MWh, and the daily average SO_2 removed by the entire FGD system was 148 tons.

During the DBA test period, of July 23 to August 24, 1984, the daily average gross generation was 9,600 MWh, and the daily average SO_2 removed by the entire FGD system was 169 tons.

SOLIDS CONTENT OF RECYCLE TANKS

The solids content (percent by weight total solids) in the recycle tanks was measured during the entire test period. Recycle Tank A consistently had the lowest total solids content during the entire test period. Recycle Tanks B and C consistently had the highest total solids content during the entire test period. During the entire test period, the average solids content in Recycle Tanks A, B, C, and D were 6.84, 11.29, 11.02, and 9.16 percent by weight, respectively.

A low solids content in a recycle tank means that water is diluting the recycle tank slurry. Water can enter the recycle tank from any or all of the following sources: presaturator flow, recycle pump seal water, limestone slurry makeup, and trap out tray bypass.

LIMESTONE STOICHIOMETRIC RATIO

A comparison of data indicates that during each phase of the test period (i.e., baseline test period and DBA test period), the average limestone stoichiometric ratio was 1.2. This means that there was no apparent savings in limestone by using DBA. IPL has demonstrated that the FGD system can be operated with good limestone utilization without additives.

SULFITE-TO-SULFATE RATIO OF RECYCLE TANK AND FILTER CAKE SOLIDS

The average molar ratio of $CaSO_3$ to $CaSO_4$ for all Recycle Tank B and filter cake samples for the entire test periods was approximately 3, which is a normal value for utility limestone FGD systems.

During the baseline test period, the average $CaSO_3$ to $CaSO_4$ ratio was 4.2 and 3.6 for Recycle Tank B and filter cake samples, respectively; whereas during the DBA test period, the ratio was 2.6 and 2.7 for Recycle Tank B and filter cake samples, respectively. A change from a baseline pH of approximately 6.0 to DBA test period pH of 5.8 resulted in more oxidation of the $CaSO_3$. Increased $CaSO_3$ oxidation at reduced pH is a normal behavior of utility limestone FGD systems.

UPPER DEMISTER SOLIDS ANALYSIS

Analyses were performed on the upper demister solids samples taken during the entire test period. Some samples represented traditional high calcium sulfate scale (long narrow crystals) formed by solubility deposition. Other samples represented solids recycle tank which most likely orginated from carry-up of solids from the scrubber absorber spray zone onto the upper demisters.

Average upper demister solids analysis during the entire test period were 67 percent $CaSO_4 \cdot 2H_20$ equivalent, 6.6 percent $CaSO_3 \cdot 1/2\ H_20$ equivalent, 4.2 percent $CaCO_3$, 4.5 percent inerts ($Si0_2$, Al_20_3, Fe_20_3, MgO), and 17.7 percent by weight absorbed water.

CORROSION CAUSED BY SCRUBBER OUTLET DUCTWORK CONDENSATE

The pH of the liquid that leaked out of the scrubber outlet damper ductwork and fell on the exterior surface of the scrubber module and platforms varied from 2.27 to 2.55. An analysis of Module D outlet ductwork condensate indicated that the iron and manganese contents of the acidic liquid were very high (i.e., Fe = 2467 and Mn = 68 ppm by weight specie), which means that the module outlet ductwork condensate corroded the ductwork carbon steel. The module outlet ductwork acid condensate leak was one of the causes of "rain" on the structural steel, platforms, exterior surface of modules, equipment, etc.

pH OF LEAKS ON TOP OF RECYCLE TANKS

The following is a representative pH of liquid leaks that fell onto the top lid of the recycle tank:

Sample	Location	pH
7-20-1A	Leak on Recycle Tank B	3.02

PRESATURATOR SOLIDS CONTENT

The solids content of the presaturator distribution plate, walls, and floor originated from electrostatic precipitator fly ash carry-through, recirculated flue gas, scrubber module splash back, and presaturator spray nozzle water. The solids buildup in the presaturator became so severe that the inlet vertical distribution plate was over 90 percent plugged and the depth of solids on the presaturator floor exceeded 2 feet.

Typical examples of the amount of solids in a presaturator are as follows. On July 22, 1984, approximately 530 buckets of solids were carried out of Presaturator D; assuming an average bucket weight of 35 lb, the total amount of solids was over 9 tons. Also on July 21, 1984, approximately 248 buckets of solids were carried out of Presaturator A which equaled approximately four tons of solids. The resulting pile of solids from Presaturator A at grade equaled approximately 65 cu ft. The cleaning of Presaturator A took approximately 8 hours using four men

The presaturators at Petersburg Unit 3 needed frequent cleaning; however, they were very difficult to clean. IPL usually used a crew of four to five personnel to shovel the solids into buckets, which were dumped to grade where they were front-end loaded into trucks.

pH OF RECYCLE TANK SLURRY

The pH measured by the (daily) calibrated pH meter in the laboratory trailer was compared with the pH noted by the scrubber control board operator at the approximate time of the sample taken by SWEC.

Comparing some of the laboratory readings with the corresponding control panel readings indicates that actual pH conditions inside the recycle tanks are usually lower than the pH indicated by the control board recorder (the signal to that recorder also controls the limestone slurry makeup valve).

The pH of the recycle tanks ranged from 4.0 to 7.7. The range was usually controlled fairly well to a relative pH variation of ± 0.5 pH unit, but the absolute value of pH, as noted above, was usually lower than recorded on the control panel. Relatively high pH values (6.3 to 6.4) usually reflect a module that has been out of service overnight and limestone allowed to dissolve without SO_2 being added. Low end values were usually a result of plugged limestone slurry feed valves which were not cleared right away. The actual pH may differ from actual conditions in the recycle tank at any time due to the pH sampling procedures used by the plant.

RECLAIM WATER pH MEASUREMENTS

Reclaim water pH measurements were taken. The normal range was 6.1 to 6.5 pH, with no substantial variation during DBA addition. One lower pH of reclaim water period occurred August 2 to August 3, 1984 (down to 5.77 and 5.85, respectively), but this was after some low pH testing (down to pH 5.3 range) of the recycle tank conditions during August 1, 1984. For the most part (except for one reading at 5.96 on August 16, 1984), the pH of the reclaim water during DBA testing was between 6.09 to 6.73, which is comparable to pre-DBA period pHs.

DEMISTER WASH WATER

Demister wash water consisted of a mixture of reclaim water and makeup water (i.e., White River water). White River water pH varied from 7.08 to 8.45 with an average of 8.1 during the test. The average total suspended solids content of the demister wash water was 1.1 percent by weight, which is considered to be very high. The average pH of the demister wash water during the entire test period was 6.3.

BOOSTER FAN MOTOR AMPERAGE AND INLET VANE SETTINGS

Between August 3 and August 8, 1984, SWEC collected data on booster fan motor amperage at various fan inlet vane settings. These were obtained by requesting the FGD system operator to call Unit 3 boiler turbine generator board operators and have them relay current amperage to SWEC.

The best fit of a linear relationship occurred above a 40 percent booster fan vane setting, so data below a 40 percent vane setting were left out of the linear regression. The linear relationship fits were reasonably good, with correlation coefficients $\Gamma = 0.9930$ for BFF-3-1 and $\Gamma = .9799$ for BFF-2.

For BFF-3-1, the relationship between vane setting and amperage draw was for vane settings between 40 and 100 percent open.

amp = 157.0495 + 3.6426 x (% vane set)
n = 12 (number of data points)
$\Gamma = 0.9930$ (correlation coefficient)
Sx = 16.35, Sy = 59.98 (standard deviations of sample)

For BFF-3-2, the following linear relationship is the best fit for vane setting vs amperage draw for vane settings between 40 and 100 percent open.

amp = 235.0277 + 2.3546 x (% vane set)
n = 13
$\Gamma = .9799$
Sx = 16.18, Sy = 38.87

The above equations document the electricity savings that can result from decreasing the amount of flue gas scrubbed. The use of DBA allows utilities to remain in compliance while scrubbing less flue gas.

CONCLUSIONS

As presented in the following sections, the maximum sulfur coal that can be burned at Petersburg Unit 3 and remain in compliance depends on many factors. DBA use improved SO_2 removal efficiency, but the short-term variability in SO_2 removal efficiency makes its use appropriate to plants with a 30-day averaging period (like that for Subpart Da units).

MAXIMUM SULFUR COAL THAT CAN BE BURNED WHEN NOT USING DBA

A review of the baseline test data indicates that Petersburg Unit 3 maintained its current 30-day average SO_2 compliance when the coal sulfur content ranged from 2.37 to 3.16 (as fired percent sulfur), under the loading and operating conditions of the test. This coal can be burned at full load if the spare recycle pumps are employed, booster fan inlet vanes are set at 85 percent, and the module pH is 6.0. The unpredictable short-term variability in SO_2 removal discussed earlier makes it difficult to predict future short-term performance. The limestone grind should be maintained at greater than 90 percent passing a 325-mesh sieve, and the limestone stoichiometric ratio (moles calcium carbonate used/moles SO_2 removed) should be approximately 1.2.

MAXIMUM SULFUR COAL THAT CAN BE BURNED WHEN USING DBA

A review of the DBA test period data indicates that the maximum sulfur coal that can be burned at Petersburg Unit 3, while maintaining its current 30-day SO_2 control and operating with 1,000 ppm by weight adipic equivalent of DBA, was in the range of 2.4 to 3.9 (as fired) percent sulfur coal under conditions existing during the test. This coal can be burned at full load and in compliance if no spare recycle pumps are employed, booster fan inlet vanes are set at 75 percent, and the module pH is 5.8. The ball mill should be operated 24 hours per day with the best grind possible (most likely less than 90 percent passing a 325 mesh). The limestone stoichiometric ratio should be approximately 1.2.

MAXIMUM SULFUR COAL THAT CAN BE BURNED AT PARTIAL LOAD WITH A SPARE SCRUBBER MODULE

IPL instituted a program to replace defective scrubber module isolation dampers. This action may result in the possibility of on-line maintenance of a spare module at near full load. Assuming the use of DBA results in over 90 percent SO_2 removal efficiency in the modules and three scrubber modules are operating, a coal in the range of 2.2 to 2.4 (as fired) percent sulfur can be burned at 500 MW, while the spare scrubber module is cleaned or maintained. DBA test data collected on July 26, 1984, is indicative of the ability of the FGD system to operate at near full load with relatively low sulfur coal, while maintaining SO_2 control using only three scrubber modules.

PERMANENT DBA SYSTEM

IPL insitituted a program to install a permanent winterized DBA system at the Petersburg Unit 3 scrubber to improve the SO_2 removal capability of the scrubber and to observe the effects of long-term use of DBA. Of particular importance are 1) corrosion of scrubber materials, 2) rates of demister pluggage, 3) effects on thickener operation at different polymer dosage rates, 4) possible changes to pumping sequences, 5) vacuum filter performance and filter cloth blinding, 6) water balance changes, and 7) effects of slurry solids content on SO_2 removal efficiency in combination with DBA.

ACKNOWLEDGEMENT

The authors would like to thank the management and scrubber operators of IPL, Monsanto Chemical Company, Acurex Corporation, Commercial Testing & Engineering Company, McKenzie Tank/Truck Lines, and Industrial Contractors, Inc. The hard work and good faith efforts by all personnel involved contributed greatly to the success of the scrubber test.

REQUIRED STATEMENT

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

REFERENCES

1. Rock Talk Manual 1982 Edition, McCormick-Armstrong Co., Wichita, Kansas, 1982, Table C-2, p. 49.

2. U.S. Environmental Protection Agency. Standards of Performance for Stationary Sources. Federal Register, 40CFR60, Methods 1 through 4, and 8, December 23, 1971 (as amended through July 1 1983).

3. U.S. Environmental Protection Agency. Federal Register, 40CFR60, Method 6, Section 4.3, Sample Analysis.

APPENDIX I
PROCEDURE FOR ORGANIC ACIDS BY BUFFER CAPACITY TITRATION

DISCUSSION

The method is not specific to adipic acid or to organic acids in general, but measures any buffering compound. Provision can be readily included (not discussed here) to correct for carbonate and sulfite buffering effects.

PROCEDURE*

Calibrate pH meter:

The pH meter should be calibrated daily using both the pH 4 and pH 7 standard buffers. Between samples, the calibration should be checked with the pH 7 buffer.

Fill burets:

(a) Put 1 N NaOH in one buret.

(b) Put 0.1 N HCl in the other buret.

Prepare sample:

(a) Put a magnetic stir bar in a clean and dry 250 ml beaker.

(b) Pipet a 100 ml aliquot of scrubber filtrate into the beaker (the filtrate should be at room temperature).

(c) Place the beaker on the magnetic stirrer, turn on the stirrer, and immerse the electrodes in the sample solution.

(d) Switch the pH meter to OPERATE, wait 1 to 2 minutes for a stable reading, and record the pH of the sample solution.

Adjust sample pH to 6:

(a) Measure the initial level of the NaOH buret to ± 0.01 ml and record as V_I,NaOH·.

(b) SLOWLY add 1 N NaOH dropwise until the pH of the sample solution is ≅6. (Because the NaOH is relatively concentrated, it will be difficult to get a pH of exactly 6.0. If this is the case, it is preferable to overshoot pH 6 slightly and titrate back to pH 6 with HCl according to step (d)).

(c) Rinse the tip of the buret into the sample with a small amount of DI water, record the final buret level as V_F,NaOH, and record the pH of the sample solution.

*This procedure is based on a general procedure developed and published by Radian Corporation. The procedure was modified slightly.

(d) If pH 6 was exceeded during the addition of NaOH, switch to HCl buret and SLOWLY add 0.1 N HCl dropwise until the pH of the sample solution is 6.00 ± 0.02. Rinse the tip of the buret with a small amount of DI water. Record the pH as pH_I.

Titrate sample to pH3:

(a) Measure the level of the HCl buret to ±0.01 ml and record as V_I,HCL.

(b) SLOWLY add 0.1 N HCl until the pH of the sample solution reaches pH 3.00 (for best results, it is desirable to obtain a final pH of 3.00 ± 0.02).

(c) Rinse the tip of the buret with a small amount of DI water, measure the final level of the HCl buret to ±0.01 ml, and record as $_V F$,HCL.

(d) Record the pH of the sample solution as pH_F.

CALCULATION

Buffer Capacity (Bc)

$$B_c \quad \frac{C \times V}{\Delta pH \times A}$$

where:

C = normality of HCl in meq/ml
V = volume HCl consumed in ml = V_F,HCL -V_I,HCL
A = sample size in 1
$\Delta pH = pH_I - pH_F$

Adipic acid equivalent (ppm by weight in solution)

Adipic acid = 236.45 (B_c - 2.1851) for recycle tank in operation.

Adipic acid = 236.45 (B_c - 1.7283) ppm for recycle tank out of service overnight.

Adipic acid = 236.45 (B_c - 1.4900) ppm for reclaim water.

Adipic acid = 236.45 (B_c - 0.993) ppm for limestone reagent slurry.

Adipic acid = 236.45 (B_c - 1.1300) ppm for demister washwater.

The above equations were developed during the Petersburg Unit 3 FGD system DBA tests of July and August 1984.

OPERATING RESULTS OF TOYAMA KYODO ELECTRIC POWER'S CHIYODA THOROUGHBRED 121 FLUE GAS DESULFURIZATION SYSTEM

K. Wataya and A. Hori
Toyama Kyodo Electric Power Company

N. Hashimoto and H. Koshizuka
Chiyoda Chemical Engineering and Construction Company, Ltd.
Yokohama, Japan

D. D. Clasen
Chiyoda International Corporation
Seattle, Washington

ABSTRACT

This paper reviews the design and initial operating experience of two Chiyoda THOROUGHBRED 121 Flue Gas Desulfurization plants installed at Toyama Kyodo Electric Power Company's Toyama Shinko Kyodo power station to treat flue gas from two 200 MW coal-fired boilers. This is the first application of the second generation CT-121 process to large electric utility coal-fired boilers.

Each CT-121 unit consists of a single scrubber and limestone slurry preparation and gypsum dewatering equipment. Each unit is also equipped with a Ljungstrom type gas-gas heat exchanger for reheating scrubbed flue gas.

Plant operation, since startup in July 1984 (Unit 1) and August 1984 (Unit 2) has been smooth and trouble free. The plants are operated at a SO_2 removal efficiency of 85 percent. Limestone utilization is greater than 99 percent and the dry, gypsum by-product is sold to cement and wallboard manufacturers. Plant reliability, including shakedown operations, has been superb, 99.9 percent for Unit 1 and 100% for·Unit 2.

Inspection of the system following shakedown operation revealed no scaling, plugging or corrosion problems. Maintenance has been limited to routine and general servicing of equipment.

INTRODUCTION

Toyama Kyodo Electric Power Company was established in March 1969 as a cooperative by Sumitomo Chemical Co., Ltd. and Hokuriku Electric Power Co., Ltd. Subsequently, three 250 MW oil-fired power plants were constructed to provide electric power for the aluminum refining industry. Although all the units were equipped with electrostatic precipitators, only Unit 1, at the time, was equipped with an FGD system.

Following the oil crisis and subsequent increase in the price of fuel oil, it was decided to convert Units 1 and 2 to burn pulverized coal having the following typical characteristics:

Heating value, Btu/lb	11,900 - 12,400
Moisture content, wt.%	3.1 - 3.8
Ash content,wt.%	12.7 - 12.9
Sulfur content, wt.%	0.5 - 1.0
Chlorine content, ppm	130 - 425
Fluorine content, ppm	20 - 80

The conversion, in addition to modifications to the two boilers, included the upgrading of the two existing ESPs, the conversion of the existing Unit No. 1 FGD system to CT-121, and installation of a totally new CT-121 system for Unit No. 2. The conversion also included for each of the two boilers, the installation of NO_x control equipment and a gas-gas heat exchanger for reheating the scrubbed flue gas. Conversion work on the two boilers was begun in August 1982 and completed in July 1984. The overall flue gas cleaning system for each boiler is shown in Figure 1.

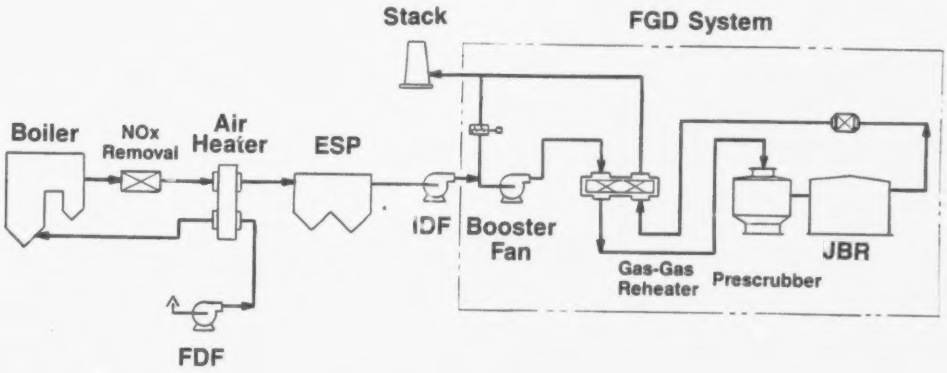


Fig. 1. Flue Gas Cleaning System

Chiyoda Chemical Engineering and Construction Company's second generation limestone/gypsum CT-121 system was selected by Toyama due to its simple design and operation, low electric power requirement, high reagent utilization, high particulate removal capability, low space requirements (an important consideration because of the retrofit nature of the project) and overall lower costs compared to first generation limestone/gypsum processes.

In addition to removal of SO_2, the two CT-121 Systems were also designed to remove 70% of the fly ash not removed by the ESPs, thereby taking advantage of the inherent high particulate removal capability of the process.

The Unit 1 System was routinely placed into service on July 9, 1984 and Unit 2 on August 23, 1984. The two systems have met or exceeded all performance guarantees (including particulate removal) and operation has been smooth and trouble free since start-up.

GENERAL DESCRIPTION OF THE CT-121 SYSTEM

Table 1 is a summary of the major design conditions for the two CT-121 systems, including the Gas-Gas Heater (GGH) and wastewater treatment sections. Table 2 is an equipment list including equipment dimensions and materials of construction.

Figure 2 shows the general arrangement of major equipment including the two stacks. Figure 3 is an overview of one of the FGD systems.

The CT-121 system, the outgrowth of Chiyoda's experience with first generation limestone/gypsum systems, represents a major improvement over first generation lime/limestone systems.

Figure 4 is a schematic of the JBR, the heart of the CT-121 Process. In the JBR, there are a number of mass transfer operations which occur simultaneously. These are:

- SO_2 transfer from the gas to the liquid-phase.
- Oxidation of liquid-phase sulfite to sulfate.
- Neutralization of sulfuric acid by addition and dissolution of limestone.
- Gypsum crystallization and growth.

As can be seen in Figure 5, a comparison of CT-121 with a typical first generation limestone/gypsum process, the JBR design greatly simplifies the overall scrubbing process. Because the process fully integrates all of the above chemical steps into a single vessel, the following equipment is eliminated.

- Slurry recycle pumps,
- Slurry spray nozzles,
- Separate reaction tanks,

TABLE 1. MAJOR DESIGN CONDITIONS

	200 MW COAL	250 MW OIL
Sulfur Content of Fuel	1.0%	1.2%
Flue Gas Flow Rate	404,000 scfm	416,000 scfm
Flue Gas Temperature	275°F	304°F
SO_2 Concentration	790 ppm(dry)	692 ppm(dry)
Particulate Loading	0.04 gr/dscf	0.01 gr/dscf
SO_2 Removal (after GGH)	80%	80%
Particulate Emission (after GGH)	$\leq$0.01 gr/dscf	$\leq$0.01 gr/dscf
Temperature (after reheater)	217°F	240°F
Reagent	Limestone	
Size	90% minus 200 mesh	
Purity	>97%	
By-product Gypsum	Saleable (wallboard grade)	
Wastewater	0 ∿ 35 gpm	
pH	5.8 ∿ 8.6	
SS	$\leq$30 ppm	
Oil	$\leq$ 2 ppm	
COD	$\leq$10 ppm	
F	$\leq$15 ppm	

TABLE 2. EQUIPMENT LIST AND SPECIFICATIONS

Equipment Name	Q'ty	Type	Dimensions or Capacity	Material
Prescrubber	1	Spray Column	33'Ø x 72'H	C.S. + FLRP
JBR	1	Cylindrical	52'Ø x 42'H	Type 316L S.S./FRP
Overflow Tank	1	Cylindrical	14'Ø x 16'H	C.S. + FLRP
Powdered Limestone Silo	1	Cylindrical	26'Ø x 27'H	C.S.
Limestone Slurry Tank	1	Cylindrical	12'Ø x 13'H	C.S. + FLRP
Mother Liquor Tank	1	Cylindrical	11'Ø x 15'H	C.S. + FLRP
Gas-Gas Heater	1	Rotating Element	33'W x 36'L x 22'H	S-TEN, FLRP Enameled Heating Element
Mist Eliminator	1	Chevron	Three-stage	C.S. + FLRP + PP
Flue Gas Fan	1	Turbo	460,000 scfm, 32 in. W.C.	S-TEN
Oxidation Air Blower	1+1S	Turbo	4,700 scfm, 8 psig	FC
Gypsum Centrifuge	2+1S	Basket	2.25 ton/hr	Type 316L S.S.
Gypsum Clarifier	1	Cylindrical	32'Ø x 10'H	
Water Cooling Pump	2+1S	Horizontal vortex	2,200 gpm	ALLOY 625
Gypsum Slurry Pump	1+1S	Horizontal vortex	200 gpm	SCS14
Limestone Slurry Pump	1+1S	Horizontal vortex	105 gpm	SCS14

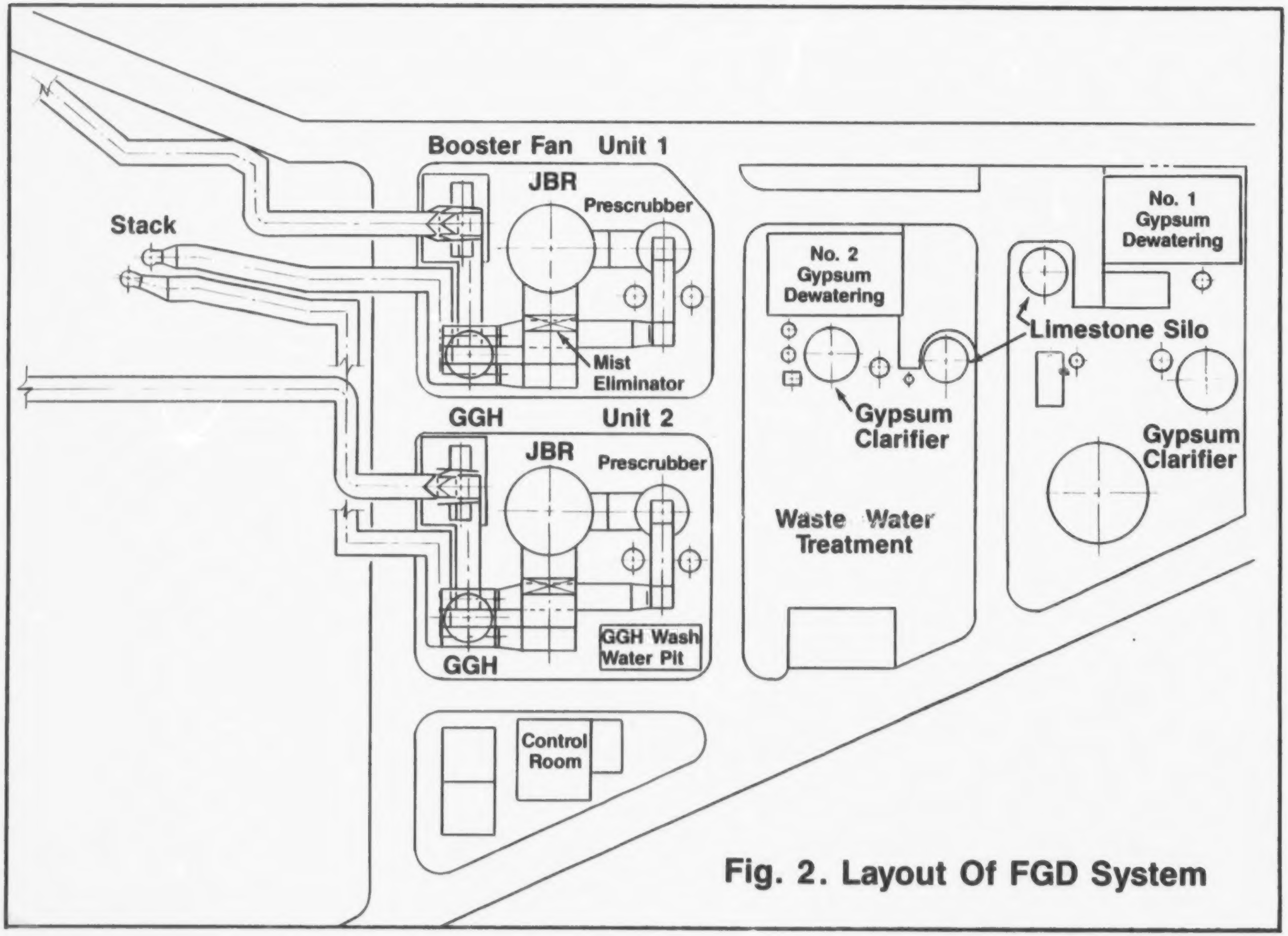

Booster Fan
Unit 1
JBR
Prescrubber
Stack
Mist Eliminator
GGH
Unit 2
JBR
Prescrubber
GGH Wash Water Pit
GGH
Control Room
No. 2 Gypsum Dewatering
Gypsum Clarifier
Waste Water Treatment
No. 1 Gypsum Dewatering
Limestone Silo
Gypsum Clarifier

Fig. 2. Layout Of FGD System

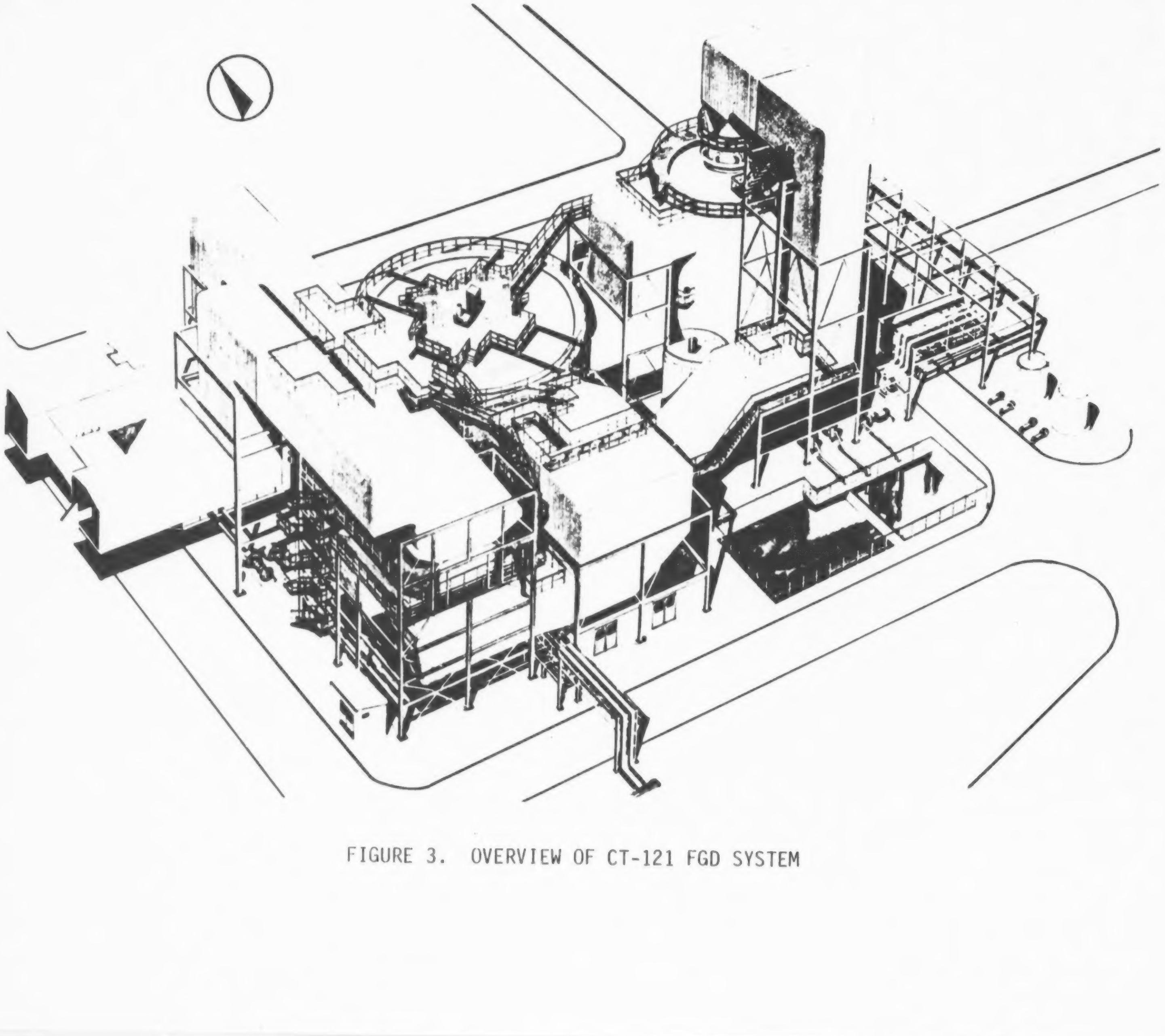


FIGURE 3. OVERVIEW OF CT-121 FGD SYSTEM

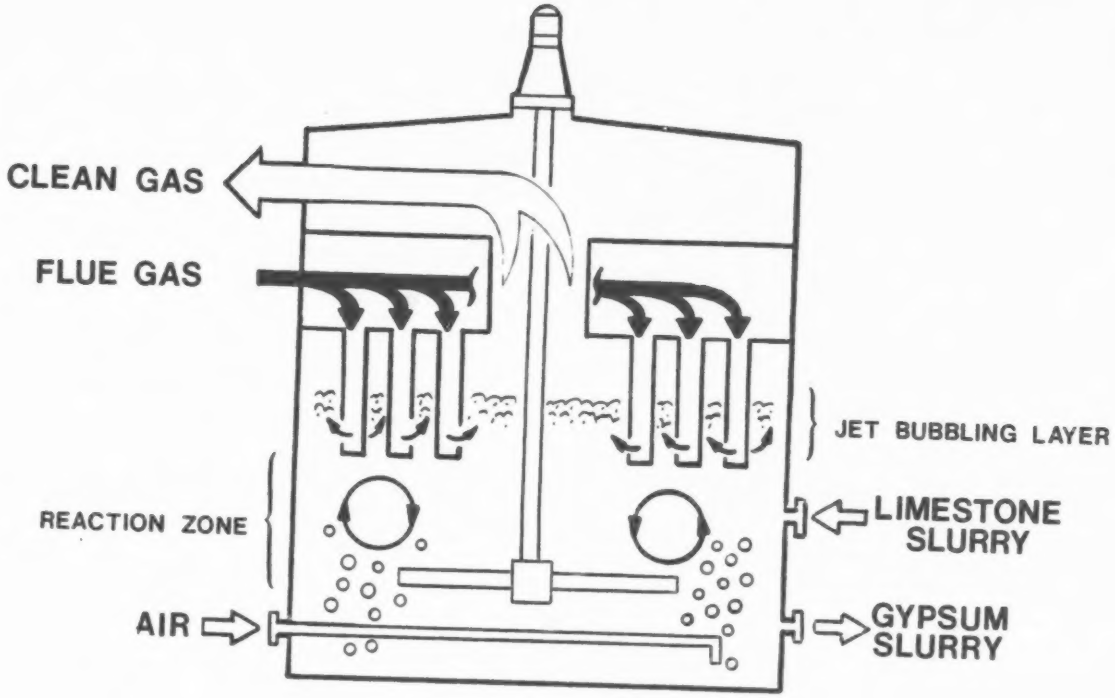
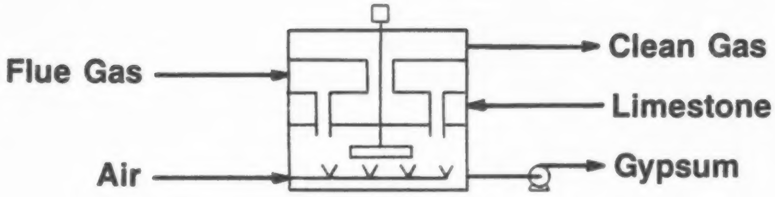

CLEAN GAS
FLUE GAS
JET BUBBLING LAYER
REACTION ZONE
LIMESTONE SLURRY
AIR
GYPSUM SLURRY

FIGURE 4. JET BUBBLING REACTOR

CT-121 Process


Flue Gas
Air
Clean Gas
Limestone
Gypsum

JBR
(Absorption • Oxidation • Neutralization • Crystalization in one vessel)

First Generation Limestone/Gypsum Process

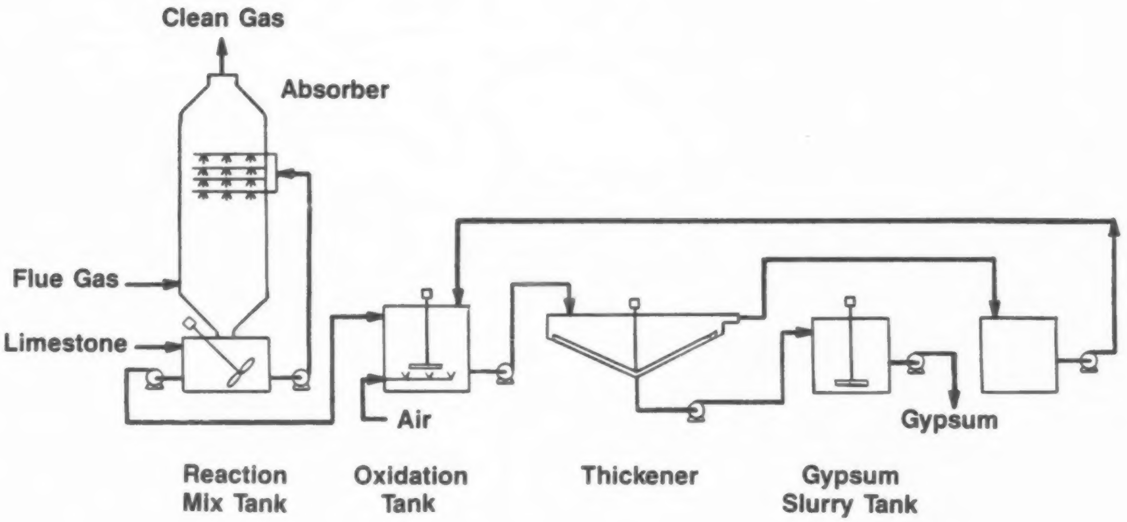

Clean Gas
Absorber
Flue Gas
Limestone
Air
Gypsum
Reaction Mix Tank
Oxidation Tank
Thickener
Gypsum Slurry Tank

Fig. 5.
Comparison Of CT-121 With
First Generation Limestone/Gypsum Process

- Oxidizer tanks,
- Thickeners or other predewatering devices,
- Ancillary equipment such as pumps, agitators, rakes, and process instrumentation.

PROCESS DESCRIPTION

A process flow diagram of the flue gas desulfurization section which is representative of both units is shown in Figure 6. The major components of the system on the gas side are a gas-gas heat exchanger for reheating the scrubbed flue gas, a prescrubber, a Jet Bubbling Reactor (JBR) which combine all the chemical process steps (SO_2 absorption, oxidation, neutralization, and crystallization) in a single vessel.

Major components on the liquid side are broadly divided into three categories: limestone slurry preparation, gypsum dewatering, and wastewater treatment. The limestone slurry preparation system consists of a powdered limestone silo, limestone feeder and a slurry tank. The gypsum dewatering system consists of 2 plus 1 spare basket type centrifuges, mother liquor clarifier, and gypsum storage. The wastewater treatment plant consists of particulate, heavy metal and fluoride removal steps.

PROCESS CHEMISTRY

The major difference between the chemistry of CT-121 and first generation limestone processes is the pH at which absorption and chemical reactions take place. Operation at a lower pH is the key to scrubbing reliably and efficiently with limestone. The basic reason is that the rate of reaction for limestone dissolution and sulfite oxidation is a function of the pH or, more specifically, the hydrogen ion concentration (for which pH is a measure). The lower the pH the greater the hydrogen and hydrogen bi-sulfite (HSO_3-) ion concentrations. As a result, the rate of reaction for limestone dissolution and oxidation of the bi-sulfite ion is greatly increased over the pH range of 3.5 to 5.0.

Major reactions that are dependent on pH are:

$$SO_2(g) \rightleftarrows SO_2(aq) \qquad (1)$$
$$SO_2(aq) + H_2O \rightarrow H_2SO_3 \qquad (2)$$
$$H_2SO_3 \rightleftarrows HSO_3^- + H^+ \qquad (3)$$
$$HSO_3^- + \tfrac{1}{2}O_2 \rightarrow SO_4^{--} + H^+ \qquad (4)$$
$$CaCO_3(aq) + 2H^+ \rightarrow Ca^{++} + CO_2 + H_2O \qquad (5)$$
$$Ca^{++} + SO_4^{--} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \qquad (6)$$

At a pH value in the range of 3.5 to 5, limestone dissolution occurs quickly and completely. The result is that all the limestone reagent goes into solution. There remains essentially no solid-phase limestone in the JBR. This not only makes it possible to achieve high reagent utilization, but also, the elimination of scaling and plugging in the mist eliminator. If there is no unused limestone in the absorbent, there can be no limestone carried over to the mist eliminator to eventually turn into hard

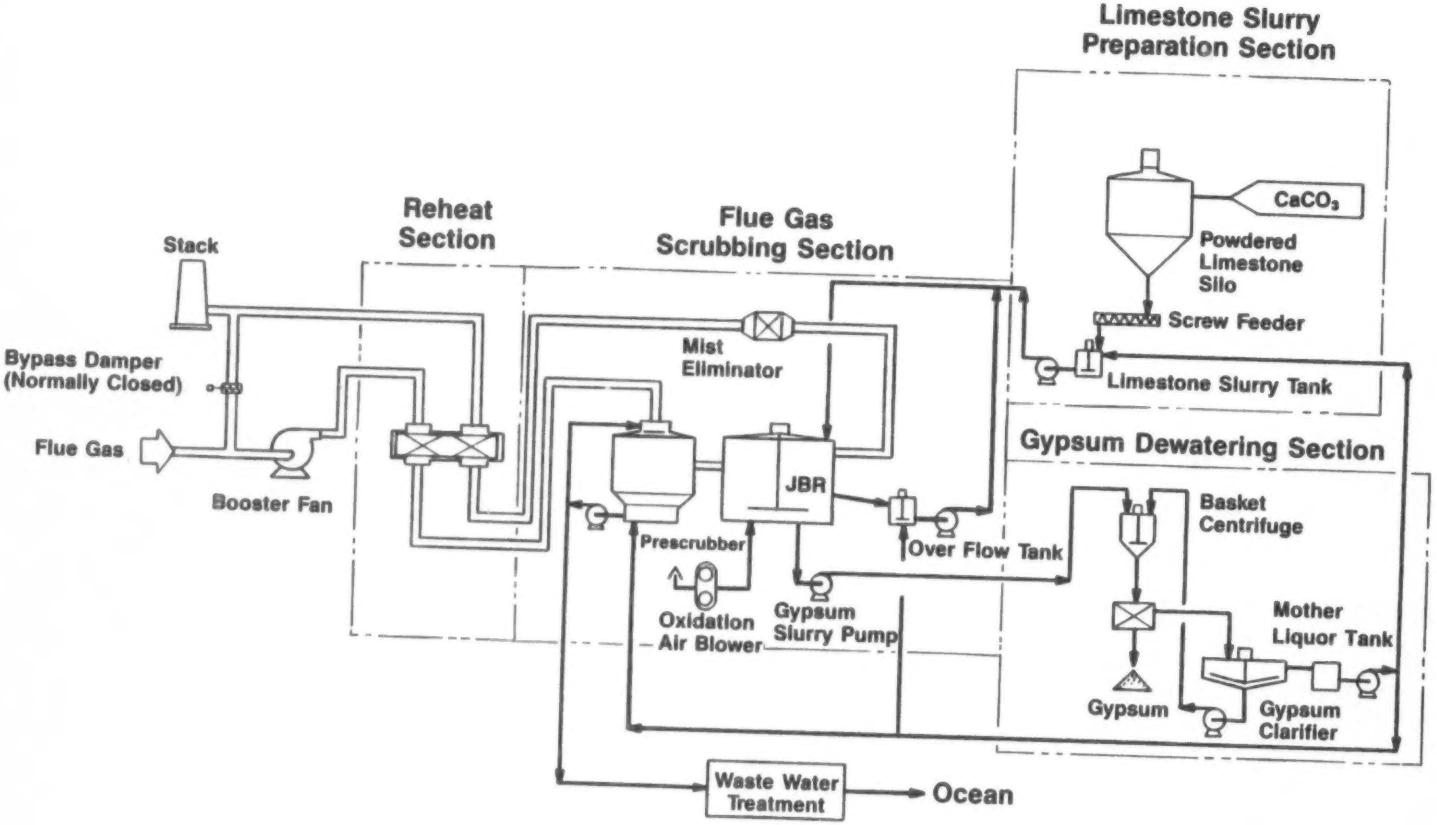

Limestone Slurry Preparation Section
CaCO$_3$
Powdered Limestone Silo
Screw Feeder
Limestone Slurry Tank
Reheat Section
Flue Gas Scrubbing Section
Stack
Bypass Damper (Normally Closed)
Flue Gas
Booster Fan
Mist Eliminator
JBR
Prescrubber
Oxidation Air Blower
Gypsum Slurry Pump
Over Flow Tank
Gypsum Dewatering Section
Basket Centrifuge
Mother Liquor Tank
Gypsum
Gypsum Clarifier
Waste Water Treatment
Ocean

Fig. 6. Process Flow Diagram

gypsum scale. Also, because the rate of limestone dissolution is so high, coarser limestone grinds such as 90% minus 200 mesh can be used without sacrificing utilization. The effect of pH on limestone dissolution for limestone based scrubbing processes is illustrated by the following basic rate equation:

$$R = k \left[C_{CaCO_3}\right] \left[C_{H^+}\right] \qquad \text{, where } pH = -\log_{10} \left[C_{H^+}\right]$$

As can be seen, the rate of reaction is significantly affected by the pH of the absorbent and is roughly proportional to the hydrogen ion concentration for systems having identical limestone concentrations. For example, the rate of reaction for limestone dissolution at a pH of 4, compared to a pH of 6, is approximately 100 times faster. The oxidation reaction, equation (4), is similarly affected as there would be a corresponding increase in the concentration of the bi-sulfite ion (HSO_3^-) associated with any increase in the hydrogen ion (H^+) concentration.

Ordinarily, operation at a lower pH would result in a significantly lower desulfurization efficiency due to a shift in equilibrium of equation (1) to the left. However, this shift in equilibrium is more than offset by the higher efficiency of the JBR absorber compared to spray towers. The reason for CT-121's higher efficiency is that the JBR's design makes it possible to totally eliminate the need for high horsepower slurry recycle pumps which are inherently less efficient than fans. This is why the overall power consumption for the CT-121 process is less than for first generation systems even though the pressure drop across the CT-121 system is significantly higher.

Operation at a lower pH coupled with a significantly larger reactor liquid residence time is why the CT-121 process achieves essentially 100% limestone utilization, virtually eliminates scaling and plugging problems, and produces a high quality, fully oxidized by-product that can be easily dewatered.

OPERATING RESULTS

The two CT-121 systems were smoothly and routinely started up on July 9, 1984 (Unit 1) and August 23, 1984 (Unit 2). Figure 7 summarizes the operating history of both the boilers and the CT-121 systems. As shown in Table 3, system reliability since startup has been 99.9 percent for Unit 1 and 100 percent for Unit 2. This reliability is all the more impressive considering that neither system is installed with spare scrubbing capacity (single scrubber for each boiler). The elimination of the need for spare scrubbing capacity is one of the reasons for CT-121's lower costs compared to first generation lime/limestone systems (conventional or forced oxidation).

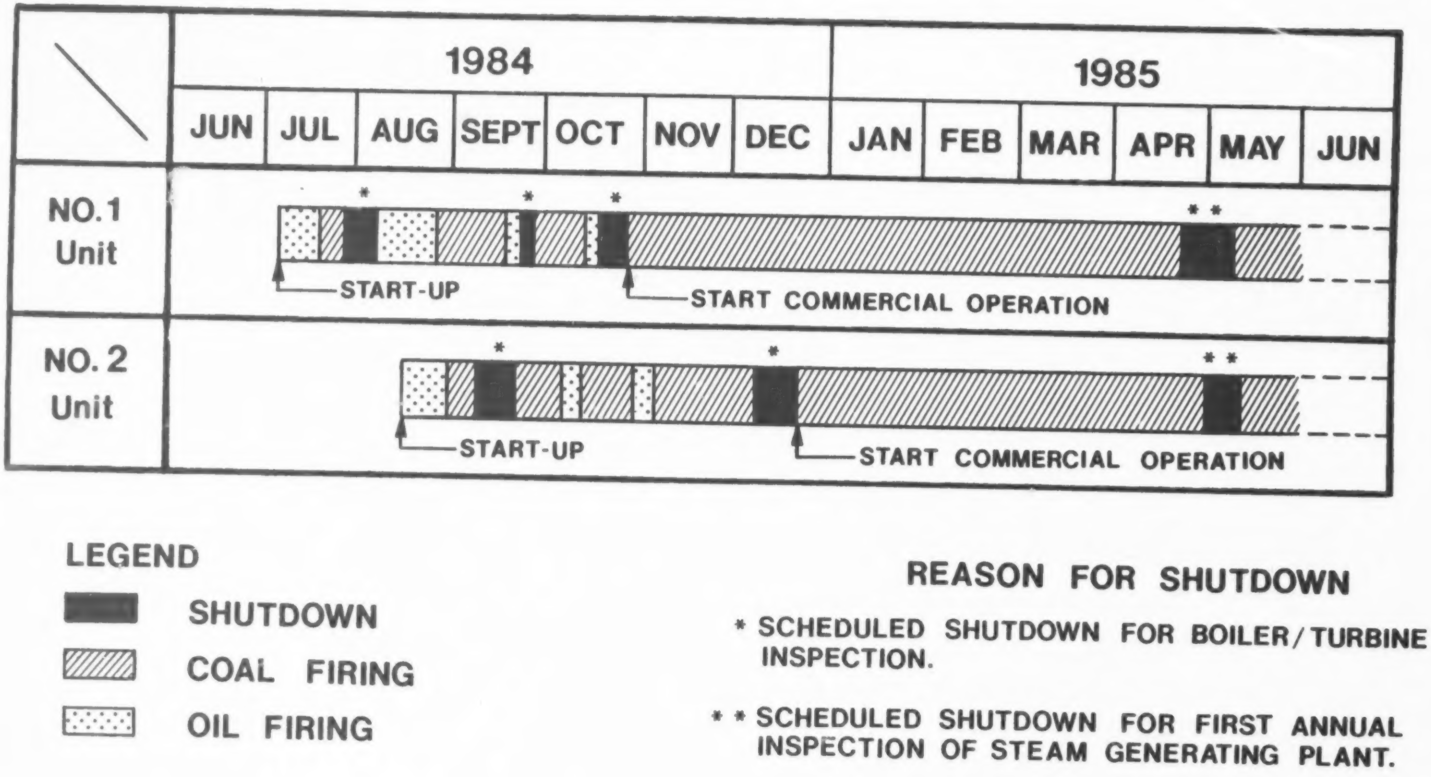


FIGURE 7

OPERATING HISTORY OF THE TOYAMA CT-121 FGD PLANTS

TABLE 3. CT-121 RELIABILITY PARAMETERS (JULY 9,1984 THROUGH MAY 30, 1985)

Parameter	Value (%)		Total Time (hours/hours)	
	Unit No. 1	Unit No. 2	Unit No. 1	Unit No. 2
Reliability[a]	99.9	100.0	5786/5792	4795/4795
Availability[b]	84.2	82.0	5792/6576	4795/5832
Operability[c]	100.0	100.0	5786/5786	4795/4795
Utilization factor[d]	88.0	82.2	5786/6576	4795/5832

---

[a] Reliability - Hours the FGD system was operated divided by the hours the FGD system was called upon to operate.

[b] Availability - Hours the FGD system is available for operation (whether operated or not), divided by the hours in the period.

[c] Operability - Hours the FGD was operated divided by the boiler operating hours in the period.

[d] Utilization factor - Hours that the FGD system operated divided by the hours in the period.

Table 4 is a summary of the performance of the CT-121 system for both coal and oil firing of the boiler.

SO$_2$ REMOVAL

The CT-121 system, because of unavoidable leakage through the GGH was designed and is operated at a SO$_2$ removal efficiency of 84 to 85% in order to achieve an overall removal efficiency of 80 percent.

A correlation showing SO$_2$ removal as a function of pressure drop is shown in Figure 8.

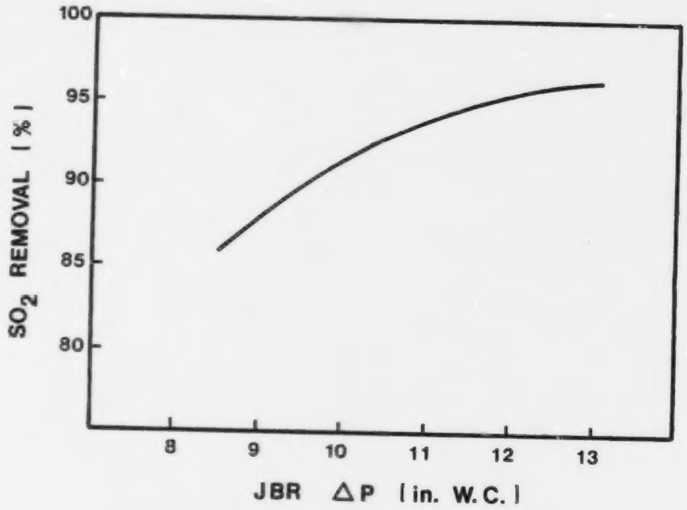


FIGURE 8. SO$_2$ REMOVAL EFFICIENCY

The SO$_2$ removal efficiency is controlled at the specified value by adjustment of the sparger submergence depth. For boiler loads or SO$_2$ loadings less than design, the submergence depth is decreased.

FLY ASH REMOVAL

The JBR, due to the jet bubbling action and higher pressure drop (similar to wet particulate scrubbers), has shown to be especially effective for removing particulate matter, including submicron particles.

The fly ash concentration at the outlet of the major components of the CT-121 system for coal firing is shown in Figure 9. The particle size distribution of the fly ash at the FGD inlet (GGH inlet) and the FGD

TABLE 4. TYPICAL PERFORMANCE OF CT-121 FGD SYSTEM

ITEM		UNIT	COAL A		COAL B	OIL
			187.5MW	200MW	200MW	250MW
Inlet Flue Gas		scfm	378,000	396,000	417,000	452,000
Gas Temp.	Inlet of FGD (Inlet of GGH)	°F	271	291	297	315
	Outlet of FGD (Outlet of GGH)	°F	234	234	234	239
SO_2	Inlet of FGD (Inlet of GGH)	ppm-d	297	340	626	664
	Outlet of FGD (Outlet of GGH)	ppm-d	38	18	101	120
SO_2 removal		%	89	95	84	85
Dust	Inlet of FGD (Inlet of GGH)	gr/dscf	0.04	-	0.004	0.003
	Outlet of (Mist Eliminator)	gr/dscf	0.001	-	-	0.001
	Outlet of FGD (Outlet of GGH)	gr/dscf	0.004	0.01	0.001	0.002
Dust removal		%	91	92	73	-
JBR pH		-	4.0	4.0	4.0	4.0
Utility	Power Consumption*	(%)	1.64	1.69	1.68	1.42
	Process make up water	gpm	84	-	92	114

*Consumption = (FGD Power Consumption/Boiler Generator Output) x 100; does not include wastewater treatment.

outlet (GGH outlet) are shown in Figure 10. As can be seen, almost all of the remaining fine particles not removed in the prescrubber are removed in the Jet Bubbling Reactor. As shown in Figure 9, 98.1 percent of the fly ash not removed in the ESP is removed in the CT-121 system. The overall removal efficiency is 97.3 percent when counting dissolved salts contained in the mist leaving the JBR. This removal is especially significant in view of the small amount of particulate matter entering the system.

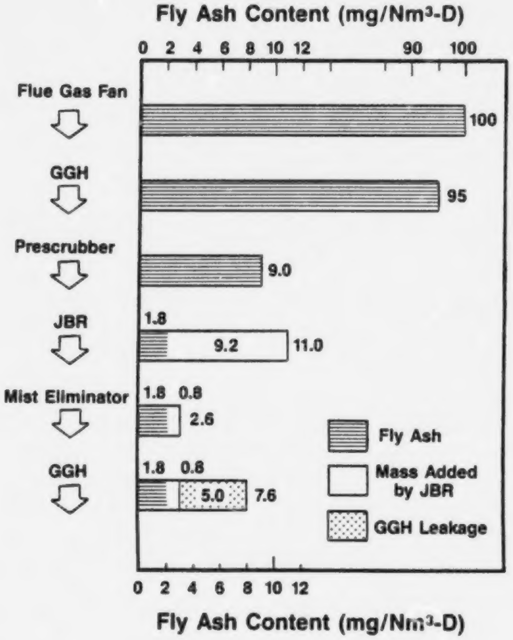


Fig. 9. Fly Ash Removal Across CT-121 For 200 MW Coal Case

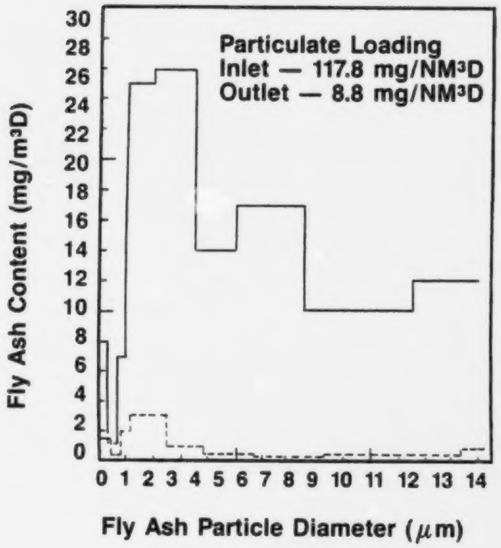


Fig. 10. Typical Particle Size Distribution At Inlet And Outlet of FGD System

Figure 9 also shows that a small amount of the particulate matter entering the GGH is caught on the rotating heat transfer element and transferred to the treated gas side as the heating element rotates between the untreated gas and treated gas.

POWER CONSUMPTION

Power consumption, during performance testing was measured at 1.42 percent of turbine generator output at design load (250MW) when firing oil and 1.68 when firing coal at design load (200MW). The consumption in both cases included total reheat costs and particulate removal in the prescrubber and JBR.

The higher power consumption for the coal-firing case is due to the larger volume of gas/kw and design requirements for treating flue gas for the 250MW oil-firing case.

The booster fan accounts for approximately 75% of the total system power consumption.

LIMESTONE UTILIZATION

Limestone utilization has averaged greater than 99%. Table 5 shows a typical analysis of the limestone used.

TABLE 5. TYPICAL LIMESTONE ANALYSIS

Chemical Composition	
$CaCO_3$	97.5 ∿ 98 wt.%
MgO	0.29 ∿ 0.4 wt.%
Al_2O_3	0.025 ∿ 0.036 wt.%
Fe_2O_3	0.094 ∿ 0.116 wt.%
SiO_2+HCl insol.	1.0 ∿ 1.25 wt.%
Particle size	90% minus 200 mesh

BY-PRODUCT GYPSUM

A typical analysis of the by-product gypsum is shown in Table 6. A photomicrograph of the gypsum crystals is shown in Figure 11. The gypsum is sold to cement and wallboard manufacturers.

MIST ELIMINATOR PERFORMANCE

The mist eliminator consists of three banks of chevron elements mounted in a horizontal run of duct located near the outlet of the JBR. The third bank was installed in order to minimize moisture carry over to the GGH and to prevent any possibility of GGH pluggage. Performance has been excellent and no scale or plugging encountered.

TABLE 6. TYPICAL GYPSUM ANALYSIS (COAL-FIRING CASE)

$CaSO_4 \cdot 2H_2O$	97.6 ∿ 98.0 wt.%
$CaCO_3$	0.03 ∿ 0.55 wt.%
MgO	0.001 ∿ 0.024 wt.%
Al_2O_3	0.005 ∿ 0.037 wt.%
Fe_2O_3	0.014 ∿ 0.096 wt.%
CaF_2	0.0012 ∿ 0.08 wt.%
HCl insol.	0.31 ∿ 1.08 wt.%
pH	6.7 ∿ 7.5
Moisture	4.2 ∿ 10.0 wt.%

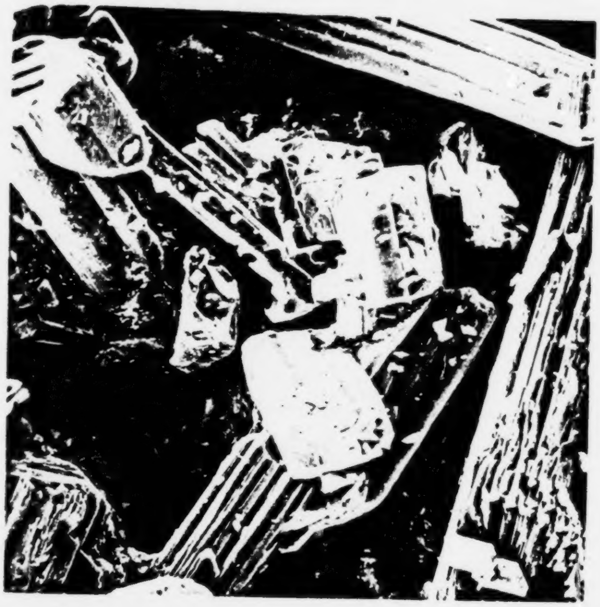


FIGURE 11. PHOTOMICROGRAPH OF GYPSUM CRYSTALS

WASTEWATER

In order to produce a saleable quality gypsum product and thereby reduce overall control costs, the FGD system must purge contaminates that would otherwise make the gypsum unsuitable for sale. In the CT-121 system, wastewater is purged from the prescrubber for this purpose. A secondary benefit of removing and purging contaminates such as particulate matter, chlorides and fluorides, in a prescrubber, upstream and separate from the absorber loop, is that the resulting low levels of corrosive constituents in downstream equipment makes it possible to use standard materials of construction such as 316 SS, thereby lowering overall system costs and increasing overall system reliability. It is significant that greater than 90% of the chlorides and fluorides are removed in the prescrubber.

Effluent from the prescrubber is discharged to the ocean after treatment with slaked lime to precipitate fluoride and heavy metals.

A typical analysis of the untreated and treated waste water is shown in Table 7. As shown the COD of the waste water, even prior to treatment, is almost nil. This is because essentially all of the absorbed SO_2 is completely oxidized in the JBR.

TABLE 7. TYPICAL WASTE WATER ANALYSIS

	Raw Water	Treated Water
pH	1.1 ∿ 1.7	6.9 ∿ 8.9
Cl	200 ∿ 4000 ppm	200 ∿ 4000 ppm
F	50 ∿ 600 ppm	5 ∿ 10 ppm
COD	<12 ppm	1 ∿ 6 ppm
NO_3	150 ∿ 350 ppm	100 ∿ 200 ppm
N-S	<1 ppm	<1 ppm

SYSTEM OPERATION AND CONTROL

The two CT-121 systems are monitored, operated and controlled from the scrubber control room. Both systems are started up and shutdown from the control room. Operation of the two systems, through the use of single-loop programmable controllers, is fully automatic.

The CT-121 system has two major control loops: flue gas control and pH control. These two control loops are schematically shown in Figure 12.

Flue Gas Flow Control Loop

The boiler load changes frequently from 25-100% of design capacity. The system responds well and automatically to such load fluctuations. The CT-121 System's response to a typical change in load is illustrated in Figure 13.

The objective of the flue gas flow control system is designed to permit smooth control of the boiler/FGD system during load changes. As shown in Figure 12, the feedforward control loop consists of a unit load sensor (FDF air flow signal) which provides the input signal for controlling the position of the inlet fan vanes of the booster fan. These vanes are positioned with an air-operated piston/cylinder actuator. A flue gas flow sensor (feedback signal), a differential static pressure sensor across the louvered bypass damper (feedback) and a logic circuit are provided for both trim adjustment to the feedforward signal and as a protective override system for opening the bypass damper in the event of a sudden pressure surge. The logic circuit is included in the programmable one-loop controllers.

The flue gas flow rate is detected by use of a turbine meter located in the duct at the inlet of the stack. This sensor, which requires back purging with instrument air to prevent deposition of fly ash, has performed exceedingly well.

pH CONTROL LOOP

The pH in the JBR is controlled by the addition of limestone slurry. The flow of limestone slurry to the JBR is controlled by the feedforward signal of the SO_2 load and unit load sensor, compensated by the feedback signal of the JBR pH and limestone slurry concentration. The limestone slurry concentration is maintained constant by adding limestone in proportion to mother liquor feed by using a proportional control loop. Limestone slurry is monitored using an in-line density meter. This control loop results in only a ± 0.3 perturbation in JBR pH for maximum load changes and in a stoichiometric ratio in the range of 1.0 to 1.01.

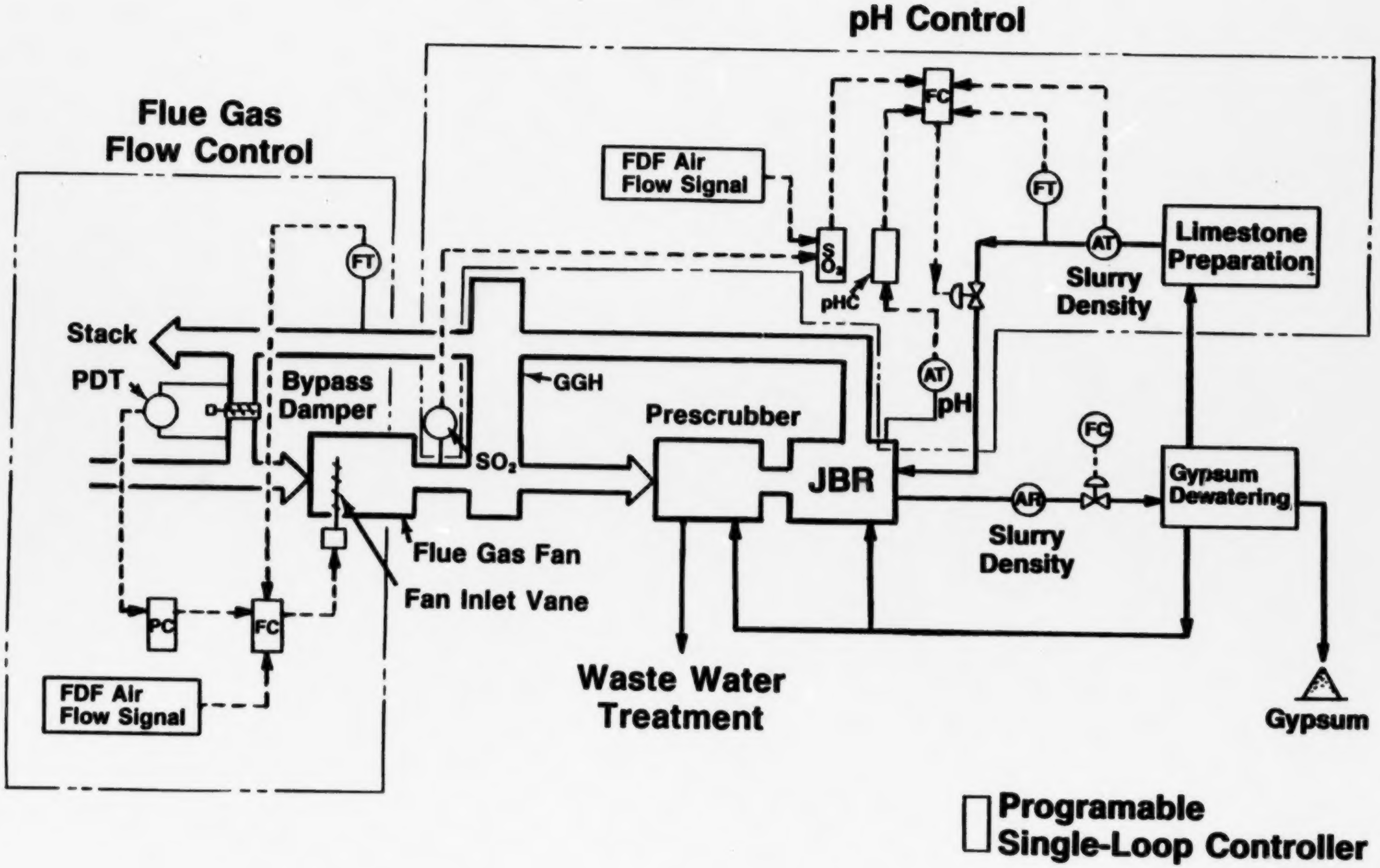

pH Control
Flue Gas
Flow Control
FDF Air
Flow Signal
FC
FT
AT
S
O2
pHC
Limestone
Preparation
Slurry
Density
Stack
PDT
Bypass
Damper
GGH
Prescrubber
AT
pH
FC
SO2
JBR
AR
Gypsum
Dewatering
Slurry
Density
Flue Gas Fan
Fan Inlet Vane
PC
FC
FDF Air
Flow Signal
Waste Water
Treatment
Gypsum
Programable
Single-Loop Controller

Fig. 12. Major Control Loops

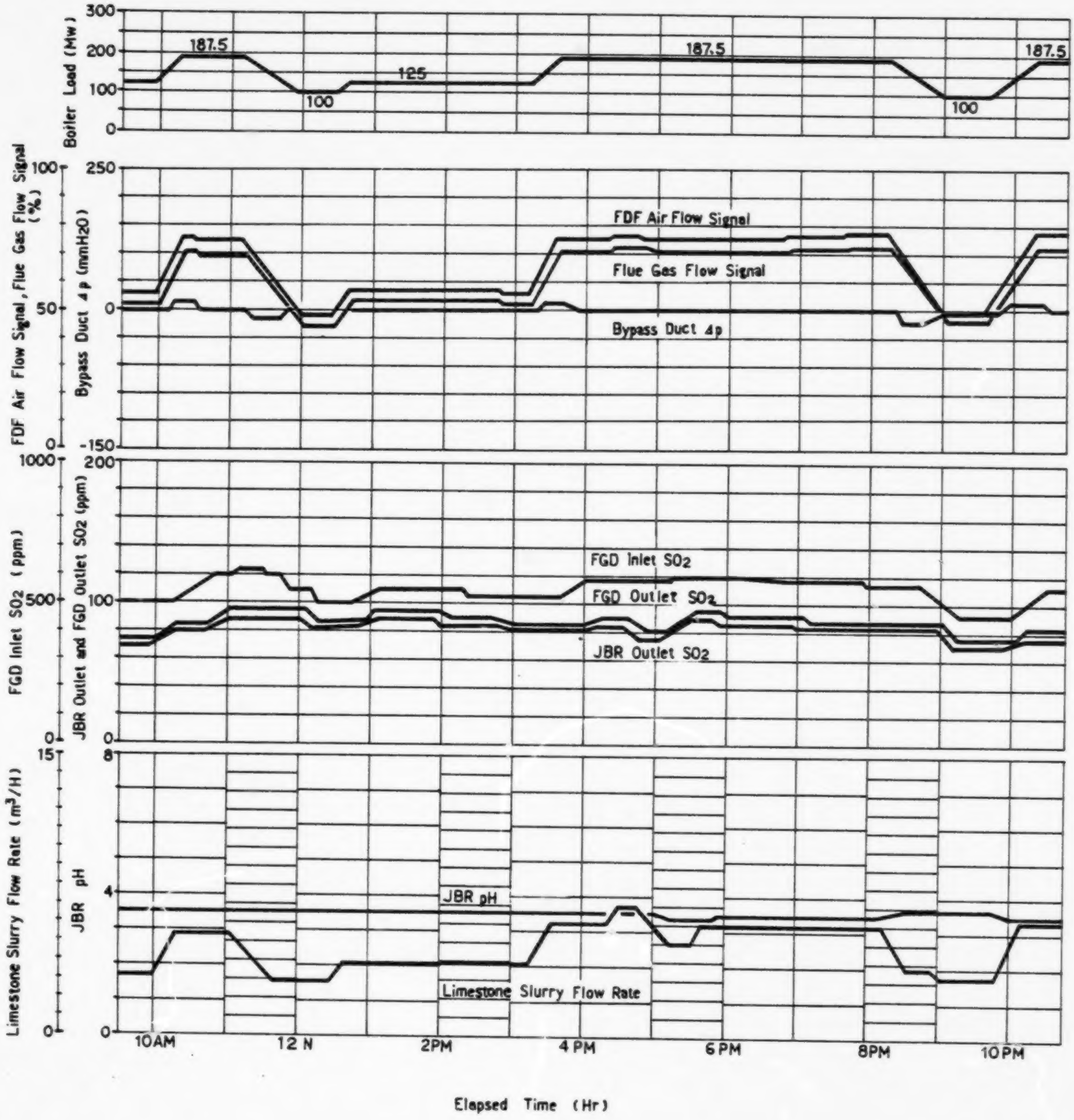


FIGURE 13

TYPICAL SYSTEM RESPONSE TO CHANGE IN BOILER LOAD (COAL-FIRING)

PERFORMANCE TESTING

Table 8 is a summary of the results of the performance testing conducted between the period of September 2 through October 19,1984 for Unit 1 and October 4 through December 1, 1984 for Unit 2.

TABLE 8. RESULTS OF PERFORMANCE TESTING

	Guaranteed Performance	Test Results	
Boiler			
Fuel	Coal	Coal A	Coal B
Generator Output, MW	200	178.5	200
Fuel S Content, wt.%	1.0	0.5	0.9
CT-121			
Overall SO_2 Removal, %	80	87.8	83.7
GGH Outlet Temp.,°F	217	234	239
Dust Emission, mg/Nm^3	30	8.8	2.5
Gypsum Moisture, wt.%	15	9.5	6.3

OPERATING AND MAINTENANCE REQUIREMENTS

Operating and maintenance functions for the CT-121 system have been minimal, and no scaling, plugging or other maintenance intensive problems have been encountered.

The personnel required for start-ups and shutdowns is less than two men. The total average requirement, including maintenance, has averaged less than one-half man per shift. Maintenance consist of the routine and standard servicing of rotating equipment. Instruments are generally calibrated and cleaned, if required, once per month.

RESULTS OF SYSTEM INSPECTION FOLLOWING SHAKEDOWN OPERATION

Unit 1 steam generating plant was shutdown in July and October 1984 for inspection. Unit 2 was shutdown in September and December 1984. During these boiler shutdowns, the CT-121 system was also inspected.

Inspection of the CT-121 system, including the JBR and the GGH, revealed no scaling, corrosion or other problems. As such, maintenance was limited to the routine servicing of equipment and the flushing off of some soft deposits of fly ash in the GGH and gypsum crystals that had accumulated on the upper deck of the JBR.

REHEAT SYSTEM

The reheat system, for this installation, is a rotary regenerative Ljungstrom type exchanger (similar to a conventional boiler air preheater). This Gas-Gas heat exchanger extracts heat from the hot inlet flue gas and transfers it to the scrubbed outlet flue gas. A general view of GGH is shown in Figure 14.

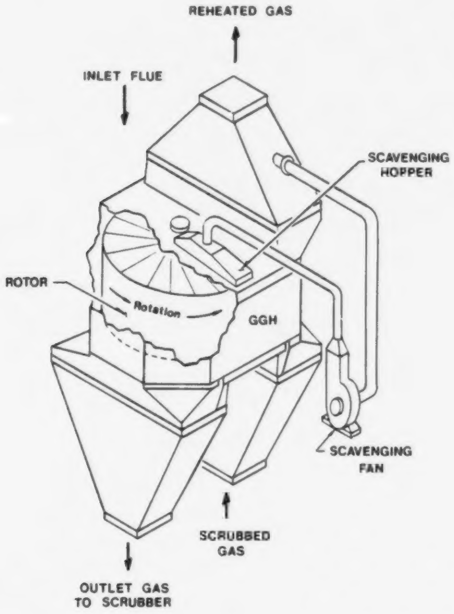

REHEATED GAS
INLET FLUE
SCAVENGING HOPPER
ROTOR
Rotation
GGH
SCAVENGING FAN
SCRUBBED GAS
OUTLET GAS TO SCRUBBER

FIGURE 14. GAS-GAS REHEATER

GAS LEAKAGE AND SO_2 REMOVAL

A small portion of the flue gas laden with SO_2 and residual particulate matter which fills the plenum of the sector between the two sector plates of the GGH is brought into the treated gas side as the rotor turns, resulting in leakage referred to as entrained leakage. A scavenging fan is used to purge entrained leakage back to the untreated gas side. Additional leakage occurs when a portion of the flue gas passes through the sealing device to the treated gas side because of the pressure differential between the untreated and treated gas streams.

The amount of overall leakage was measured by SO_2 detecting instruments. These measurements indicated that the leakage of untreated flue gas to the treated side was approximately 2.5-3.5 vol.% of the inlet flue gas. To compensate for this anticipated leakage, the CT-121 system was designed for a slightly higher SO_2 removal efficiency.

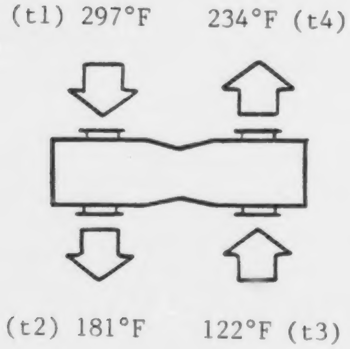
Dust leakage must also be accounted for in the overall system design.

THERMAL EFFICIENCY

The GGH system is designed to achieve an exit gas temperature of 217°F for 200 MW coal-firing and 239°F for 250 MW oil-firing. Results of performance testing of the GGH are summarized in Table 9.

TABLE 9. GAS-GAS REHEATER PREFORMANCE

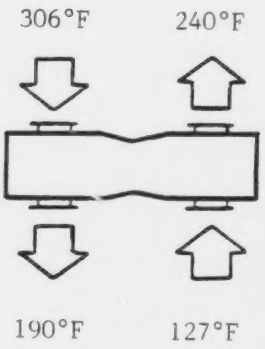
200 MW COAL CASE



Design Eff.* = 0.62

Performance = 0.64

250 MW OIL CASE



Design Eff.* = 0.62

Performance = 0.63

---

*Thermal Efficiency = (t4 - t3)/(t1 - t3)

Session 4, Part I: FGD RELIABILITY IMPROVEMENT

Dorothy A. Stewart, Chairwoman
Electric Power Research Institute
Palo Alto, CA

THE SULFUR DIOXIDE REMOVAL SYSTEM IMPROVEMENT PROGRAM AT SEVEN UNITS OF LOUISVILLE GAS AND ELECTRIC COMPANY

by: M. L. McInnis
Louisville Gas and Electric Company
P.O. Box 32010
Louisville, KY 40232

D. A. Froelich, P.E.
S. A. Bjorklun, P.E.
G. M. Graves, P.E.
Burns & McDonnell Engineering Company
P.O. Box 173
Kansas City, MO 64141

ABSTRACT

During the early part of 1983, Louisville Gas & Electric Company (LG&E) implemented a program to upgrade their mid-1970 vintage sulfur dioxide removal systems (SDRS) to current design standards. The goal of the project was to improve SDRS reliability to a minimum level of 90 percent while reducing excessive operating and maintenance expenses.

This program is at its midpoint, with design and construction proceeding at the Mill Creek Station. Problem identification and engineering recommendations are in the evaluation stage for two of the units at Cane Run. Design is proceeding for the third Cane Run unit. This paper will summarize the project scope and highlight the unique problems encountered with the SDRS improvement program.

BACKGROUND

In 1973, LG&E initiated an ambitious and capital intensive program to control the sulfur dioxide emissions from its electric generating units. This program was based upon continued use of local, high-sulfur Kentucky coal. Currently seven sulfur dioxide removal systems are in operation treating the flue gas generated from 2178 megawatts of generating capacity.

Much of the design for all seven units was performed during the early development of SDRS technology (see Table 1). Many of the inherent problems of first generation technology showed up on each of these units. Some of the major problems included corrosion, abrasion, and plugging of absorber internals and piping systems. Mechanical difficulties included operational problems with pumps, dampers, and valves. Freezing problems were also prevalent. The instrumentation and controls were overly complex, and in many cases, made SDRS operation difficult.

TABLE 1. LOUISVILLE GAS & ELECTRIC CO.
SDRS IMPROVEMENT PROJECT
SYSTEM DATA

Unit	Unit Rating	SDRS Start-Up	Absorber Manufacturer	Absorber Type	Reagent
Mill Creek 1	321	1981	Combustion Engineering	Spray Tower	Lime or Limestone
Mill Creek 2	338	1982	Combustion Engineering	Spray Tower	Lime or Limestone
Mill Creek 3	412	1978	American Air Filter	Mobile Bed	Lime
Mill Creek 4	496	1982	American Air Filter	Mobile Bed	Lime
Cane Run 4	170	1976	American Air Filter	Mobile Bed	Lime
Cane Run 5	181	1977	Combustion Engineering	Spray Tower	Lime
Cane Run 6	260	1979	Combustion Equipment Associates	Tray Tower	Soda Ash/Lime

To achieve 90 percent SDRS reliability (reliability being the number of hours the SDRS is operating divided by the number of hours it is called on to operate), the scope of the improvement program included all equipment from the ID fan outlet to the top of the chimney, all carbide lime handling systems, fresh water supply, process return water, and sludge thickening. Support systems evaluated included stack plume reheat, mist eliminator wash, slurry recirculation, thickeners, and instrument air. Electrical supply and control modification were also an integral part of the program.

PROGRAM METHODOLOGY

In developing a methodology for problem solving, it was necessary to avoid an approach of simply treating symptoms of more complex problems. Instead, the program was directed to identification and solution of "root-cause" process and design problems that result in reduced reliability.

Reports

Following an assessment of program goals and a review of the entire SDRS process, recommendations were issued in the form of an overall system report and specific subsystem reports. Each report was based upon the following:

- Performance testing.
- On- and off-line inspections.
- A review of the original design.
- Interviews with LG&E engineers, operators, and maintenance personnel.
- A review of historical reliability data.

The first report for each SDRS discusses the overall system process and makes preliminary recommendations concerning removal strategy and system chemistry. This report also makes materials of construction recommendations for absorber internals. Once an overall approach is established, other system reports are generated for each absorber subsystem such as slurry recirculation, stack plume reheat, and thickener.

Included in each report is an economic analysis. Cost estimates for equipment and materials, along with labor costs for installation, are furnished for each alternative. Operational costs for power, fuel, maintenance, and reagent consumption are also included. Finally, the present value cost for each alternative is determined. Based upon the present value analysis and the anticipated improvement in the reliability associated with each alternative, a recommendation is made.

Mill Creek Station

Mill Creek Units 1 and 2 were the first two systems evaluated. Both of these open spray tower systems are capable of operation with a lime or limestone reagent. The units have not required extensive modification. Recommended work included new isolation dampers and modifications to the process discharge and reheat systems.

The changes required for the Unit 3 SDRS are the most comprehensive at the Mill Creek Station. The first major area of change involved removal strategy. Unit 3 was originally designed and operated as a lime-based mobile-bed absorber. The beds were filled with contact spheres and continually caused pressure drop problems due to pluggage with scale and slurry. As a prerequisite to high reliability, the mobile beds had to be eliminated.

Reagent supply also influenced the design of Mill Creek 3. LG&E's supply of carbide lime is limited. To conserve lime for use at the Cane Run Station, LG&E elected to modify Mill Creek Units 3 and 4 to operate with limestone. Because the existing absorber modules were of adequate height and cross-sectional area, it was determined that the Unit 3 liquid-to-gas ratio could be increased for operation as an open spray tower utilizing limestone as the reagent.

These decisions prompted a number of significant modifications. Essentially, a new absorber had to be designed for which the critical design constraint was the existing absorber velocity. Variable parameters included liquid-to-gas ratio and slurry distribution. To determine these parameters, operating experience along with absorber simulation models were employed. Additionally, an absorber gas flow model study was conducted to help redesign the inlet duct for improved flue gas distribution.

The design constraints prompted many equipment changes. The slurry recirculation system is being replaced, including new recycle pumps, valves and piping. A new system of internal spray headers and nozzles is required. Both the increase in liquid-to-gas ratio and the conversion to limestone have had detrimental effects on reaction tank residence time. Fortunately, the size of the existing tanks was adequate to accommodate the change.

Corrosion and abrasion concerns prompted extensive modifications relating to materials of construction. Materials which experienced problems included:

- Gunite-lined absorber walls.
- FRP spray headers and recycle piping.
- Carbon-steel reheat tubes.
- 316 stainless steel nozzles.
- 316 stainless steel mist eliminators.

Replacement material selections were based on performance evaluations of their suitability as demonstrated at other operating FGD systems. The absorber inlet quench area is now being clad with alloy C-276. The module walls are being clad with a 317L (4.25 percent minimum Molybdenum) stainless steel. The new internal spray headers are also 317L (4.25 percent minimum Molybdenum) stainless steel, but are of a greater thickness than the wall cladding due to the combination of abrasion and corrosion forces that internal spray headers are subjected to. The absorber chevrons were replaced with fiberglass materials.

The final materials change involves the concrete reaction tanks. Due to the lower operating pH of a limestone system, the tanks are being coated with an epoxy-type system with fiberglass reinforcing mat. In addition, because of significant corrosion problems with structural steel, cable tray, conduit, piping and equipment located around the open topped reaction tanks, covers are being installed.

A number of mechanical changes have also been required at Unit 3. These include inlet, outlet, and bypass dampers, all support system pumps, and most piping. Reaction tank mixers have required a significant refurbishment program. Generally, the mechanical failures resulted from marginal equipment designs.

Finally, the SDRS control system is being completely redesigned. The original system was "hard wired," and included several extremely complicated control schemes. Experience showed these complicated control schemes to be unnecessary for well-tuned pH, density, and level control. A decision was made to incorporate the use of a distributed control system which will allow programming of simplified digital and analog control schemes. For example, a simple feedback loop without feedforward signals will be employed for pH control.

Conversion of the control system also allows the station SDRS control room to be relocated in the absorber area. Previously, the absorber controls were located in the main control room on the operating floor of the service building. Relocation of the control room places the operators closer to the process they are controlling.

The modifications for Mill Creek 4 are similar to Mill Creek 3 due to the similarity of original design. The absorber is being converted from a mobile bed to a spray tower design capable of operating with a limestone reagent. Since the existing pumps have adequate capacity, replacement of the recycle pumps on Mill Creek 4 is not required. This unit is also being converted from a hard-wired to a distributed type control system. Mechanical modifications for Mill Creek 4 include damper replacement, reheater upgrades, and thickener underflow pump replacement.

Cane Run Station

Most reports for the Cane Run units have not yet been written since testing and inspections are still in progress. Several major decisions, however, have been made, which will dictate much of the design for these systems.

The most significant decision concerns the reheat systems at all three Cane Run units. Units 4 and 6 have direct-fired reheat utilizing fuel oil, while Unit 5 employs an in-line steam system. These reheat systems were originally installed to provide corrosion protection for downstream equipment including the outlet ductwork and stack. The reheat was not required for plume dispersion or visibility concerns.

As with many flue gas reheat systems, these systems constituted a more significant cause of reliability problems. Because of this, analysis was performed for each unit to determine if an economic advantage existed for eliminating the reheat systems. Costs of reheat included the present value costs of steam or oil and the additional costs for maintenance. The cost of eliminating reheat, or of incorporating a wet stack design, included replacement of the failed outlet ductwork with corrosion-resistant materials. Analysis indicated the elimination of reheat would result in extremely attractive payback periods.

In addition to the economic incentive, analysis predicted that elimination of reheat would result in higher reliabilities. Based on the short economic paybacks and the potential for improved reliabilities, LG&E decided to eliminate reheat and adopt a wet stack approach. This decision added significantly to the project scope, requiring relining of all outlet ductwork with stainless steel, and relining all three stack liners with a high molybdenum-nickel alloy.

A second major requirement prompted by the wet stack decision relates to the flue gas draft system serving Unit 5. Because Unit 5 was a retrofit SDRS, a booster fan was required to account for absorber pressure drop. The fan was put on the absorber outlet to provide negative pressure at the absorber modules. Unfortunately, the booster fan has experienced serious materials problems.

When Unit 5 is modified for wet stack operation, overall pressure drop will be reduced by reheat tube removal and redesign of the outlet ductwork. With this reduction in pressure drop, the ID fans can be upgraded to accomplish the required absorber module draft for open spray towers. This means that the modules are being converted to positive pressure. While this change requires minor modifications, it is not expected to create any difficulties.

Other major decisions for the Cane Run units involve Unit 6, the dual-alkali system. Design of modifications for Cane Run 6 is underway. The primary modification involves improvements to the sludge thickening and dewatering process. The thickener operation will be converted from a batch to a continuous operation. This modification involves replacement of the thickener underflow pumps and conversion of the current secondary regeneration reactors to storage tanks for the thickener underflow. It was determined that the residence time in these tanks contributed little toward the formation of crystals with good dewatering characteristics, and that the tank mixing resulted in significant crystal degradation. Use of these tanks as vacuum filter feed tanks will provide a more consistent product for dewatering operations. Vacuum filter operating procedures are being established to improve cake washing efficiency. This change should result in significant soda ash savings. The waste treatment (sludge fixation) system equipment is being modified to reduce the current excessive maintenance requirements. Finally, internal contact trays in the absorbers will be modified to reduce system pressure drop, which currently limits unit load.

OVERVIEW

The Louisville Gas & Electric Company's Sulfur Dioxide Removal System Improvement Program is one of the largest renovation projects ever undertaken in the power industry. The goal of the program is to improve SDRS reliability to above 90 percent while reducing operation and maintenance expenses.

The modifications being implemented by the improvement program vary widely for the seven units involved. Mill Creek 3 has required a complete renovation. The reheat systems on the three Cane Run units are being eliminated. Several process modifications are required on Cane Run 6 to improve dewatering operations. Other than damper replacement and the installations of reaction tank covers, Mill Creek 1 and 2 have required only minor modification.

The problems LG&E has experienced with their sulfur dioxide removal systems are typical for the first generation technology implemented in the early 1970s. With the SDRS Improvement Program, LG&E is taking a major step toward eliminating those problems.

* * * * *

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the agency and no official endorsement should be inferred.

IMPROVING THE RELIABILITY OF INDIANAPOLIS POWER & LIGHT COMPANY'S PETERSBURG 3 LIMESTONE FGD SYSTEM

By: J. David Colley
Radian Corporation
Austin, Texas

Steve Wolsiffer
Indianapolis Power & Light Company
Petersburg, Indiana

Dorothy Stewart
Electric Power Research Institute
Palo Alto, California

Richard Rhudy
Electric Power Research Institute
Palo Alto, California

David Balfour
Radian Corporation
Austin, Texas

ABSTRACT

Preliminary results of a comprehensive program to improve the reliability of Indianapolis Power and Light Company's Petersburg 3 FGD system are presented. The objective was to identify the causes of the process problems and recommended solutions to the system's reliability problems. FGD operating guidelines developed from the information gathered during on-site testing are given. Severe mist eliminator scaling was investigated, and recommended procedures were to select better control instrumentation for the scrubbers, to determine proper operating setpoints for pH and density and to modify the mist eliminator wash system. Other testing and modifications to the system are: 1) to install and document operation of three different mechanical seals for recycle pumps, 2) to modify limestone grinding circuit, then install a particle size monitor to determine if the monitor can indicate circuit maintenance frequency, 3) to optimize adipic acid use as other process changes are made, and 4) study the problem of stack opacity as process modifications are implemented.

INTRODUCTION

The Electric Power Research Institute has several projects with the major objective of defining causes of poor reliability and maintenance problems in flue gas desulfurization (FGD) systems. Indianapolis Power and Light Company agreed to participate at the Petersburg Generating Station in two of these projects, RP2248-1, Chemical Process Problems and RP2535-1, Mist Eliminator Performance.

The problems to be investigated are marginal SO_2 removal, poor limestone utilization, mist eliminator scaling, solids carryover to outlet duct, system water balance, and stack opacity. The initial investigation at the Petersburg station has been completed and some recommended modifications are being done. Plans for future tests are also included in this paper.

BACKGROUND

The wet limestone scrubber system installed with IPL's Petersburg Unit 3 was the state-of-the-art design in 1975 and was placed in service in late 1977. The 4-module system is located downstream of cold-side electrostatic precipitators and includes two 3000 HP flue gas booster fans to the FGD system with an open-bypass gas duct configuration. The absorber equipment layout is symmetrical and mirror imaged about the centerline of the stack with vertical gas flow through the towers. One level of sprays directs slurry down. Scrubber outlet gas passes thorugh horizontal mist eliminators before it is mixed with air from an indirect ambient-air reheater. This scrubber is equipped with one full-size ball mill, one thickener, and the waste is stabilized as Pos-O-Tec (CSI, Inc.) and landfilled on site. The process is operated with a closed loop water-balance. The original turbulent contact absorber (TCA) was designed for 4.5% S coal and included a mobile packing of 3 million spheres like ping pong balls installed in three layers. IPL has modified this "obsolete technology" due to high operating costs, gas flow control problems and a high potential for scaling and module pluggage. A mobile packing design is no longer offered by any leading scrubber manufacturer.

Major equipment revisions or additions prior to 1985 have included: enclosures, pumps, mobile packing removal, installation of 3 levels of sieve trays to replace the spheres, and wholesale changeouts of fiberglass pipe, linings, dampers, nozzles, and valves. The major remaining equipment problems are with materials of construction because of corrosion.

Process and operation revisions have been tested over the past 5 years as the relaibility of individual subsystems improved. With the absorber gas liquid contact area reduced (balls removed & trays installed), the scrubber's capability has been reduced so that the system can only handle about 3.5% as-received sulfur fuel rather than the 4.5% in the original design. Limestone grind fineness had been increased in an attempt to improve limestone utilization. The pH control point was elevated to increase SO_2 removal because of marginal tower design, but a reduced limestone utilization resulted despite the finer size. Process and minor piping revisions to the original mist eliminator wash scheme were completed, but wash water saturated in gypsum was still used much of the time. Dibasic acid was tested in 1984 to further improve SO_2 removal and limestone utilization.

The major remaining operational problems at the start of 1985 were mist eliminator scaling, the potential for wet gas recirculation through the booster fans, marginal SO_2 removal, and periods of high visual stack opacity with all other emission parameters in compliance. Mist eliminator scaling and the resultant excessive moisture carryover has forced scrubber booster fans and modules out of service for high pressure water jet cleaning. Marginal SO_2 removal has forced derates on the generating unit to stay in compliance when fuel sulfur content is above 3.2%.

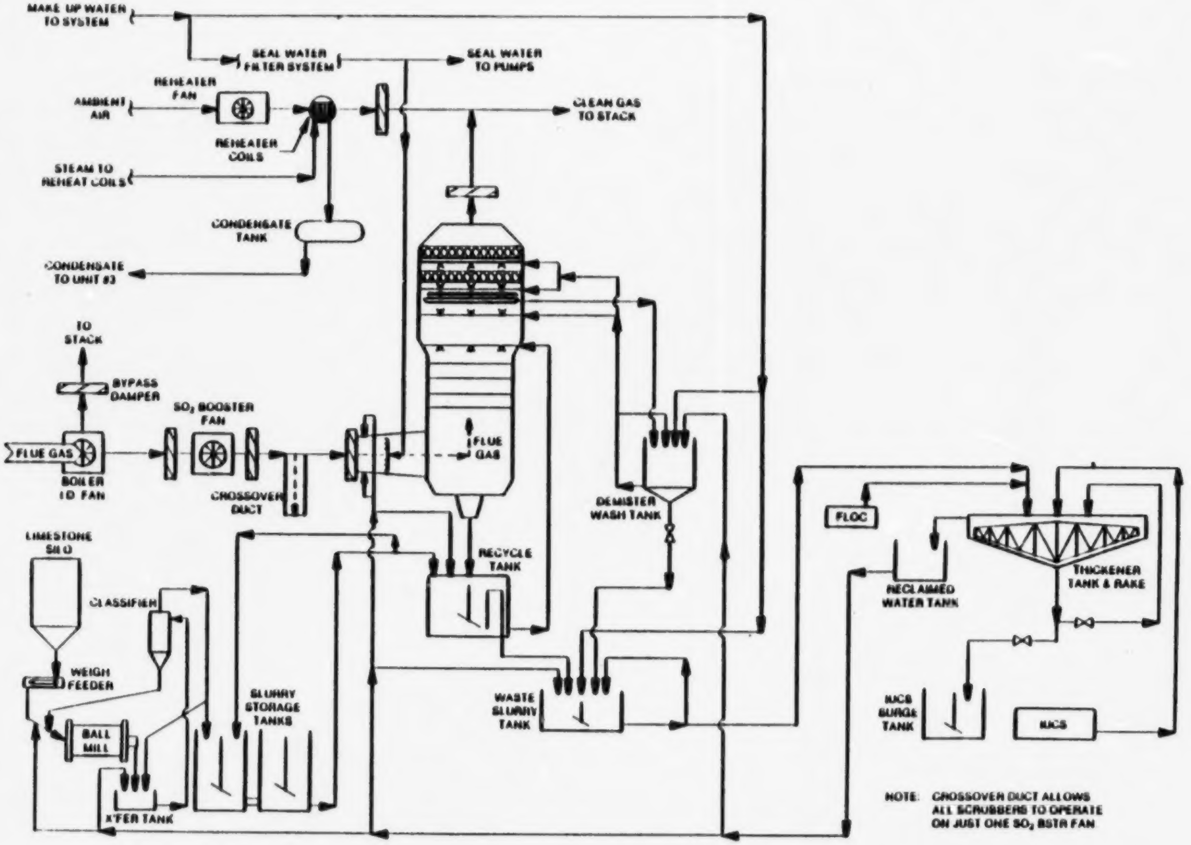
SYSTEM DESCRIPTION

Unit 3 at the Indianapolis Power and Light Petersburg generating station is a 530 megawatt base loaded boiler which began commercial operation in December 1977. The boiler fires a bituminous coal whose heating value is about 11,000 Btu/lb and whose sulfur content typically varies from 2.0 percent to 3.5 percent. The boiler supplier was Combustion Engineering. Two cold side Research-Cottrell precipitators limit particulate emissions values to less than 0.10 lbs/MMBtu. Fly ash collected in the precipitators is conveyed to the scrubber dewatering facility where it is mixed with dewatered sludge and sent to an on-site landfill. The precipitators are rated at 983,000 acfm at 279°F each for a total gas treating capacity of 1,986,000 acfm.

Figure 1 is a flow diagram of the Petersburg 3 FGD system showing one of four towers. From the ESP's, the flue gas passes through one of two boiler ID fans which supply the energy to overcome a part of the FGD system pressure drop. The FGD system was supplied by UOP Air Corrections Division. The system consists of four 25 percent capacity scrubber towers with no spare gas scrubbing capacity. Two booster fans provide the remainder of the energy to move the gas through the towers and to the stack. There are provisions to bypass gas for reheat by varying the booster fan inlet vane position. In addition, there are two indirect reheat systems which heat air with steam coils and inject it into a mixing chamber where it combines with treated flue gas before joining the bypassed flue gas.

The design gas treatment capacity of each tower is 390,000 acfm at 125°F and saturated with water (13.4 percent moisture). Design SO_2 removal efficiency is 86 percent with an inlet SO_2 concentration of 3469 ppm (dry) and at a tower pressure drop of 9.5 inches of H_2O.

The towers were originally designed and operated as turbulent contact absorbers (TCA's) with three levels of plastic spheres for improving gas-liquid contact and SO_2 removal. The TCA stages have been replaced with three levels of stainless steel sieve trays in each tower. Overall tower pressure drop remains the same.


MAKE UP WATER TO SYSTEM
SEAL WATER FILTER SYSTEM
SEAL WATER TO PUMPS
REHEATER FAN
AMBIENT AIR
REHEATER COILS
CLEAN GAS TO STACK
STEAM TO REHEAT COILS
CONDENSATE TANK
CONDENSATE TO UNIT #3
TO STACK
BYPASS DAMPER
SO_2 BOOSTER FAN
FLUE GAS
BOILER I.D. FAN
CROSSOVER DUCT
FLUE GAS
DEMISTER WASH TANK
FLOC
LIMESTONE SILO
CLASSIFIER
RECYCLE TANK
THICKENER TANK & RAKE
RECLAIMED WATER TANK
WEIGH FEEDER
BALL MILL
SLURRY STORAGE TANKS
WASTE SLURRY TANK
IUCS SURGE TANK
IUCS
X'FER TANK

NOTE: CROSSOVER DUCT ALLOWS ALL SCRUBBERS TO OPERATE ON JUST ONE SO_2 BSTR FAN

Figure 1. Flow diagram of Petersburg 3 FGD system.

Limestone is used for reaction with the absorbed SO_2. The limestone addition rate to each tower is controlled based on pH. The reaction tanks are each 280,000 gallons in capacity. The design slurry recycle rate is 23,600 gpm per tower. The tower liquid-to-gas ratio is 60 under design flow conditions. There are three recycle pumps per tower with two operating and the third for spare. The pumps were supplied by Denver Equipment Company.

The flue gas exits the gas-liquid contact section of the tower and first passes through the mist eliminator wash trap out trays which serve to segregate mist eliminator wash water from the recycle loop. The gas next passes through the mist elimination section which consists of two banks of chevron type mist elininators. The first bank is a three-pass design and the second bank is a four-pass design. The front and back sides of the first bank are washed continuously with a combination of fresh water, thickener overflow, and trap out tray return water. The front side design wash rate is 400 gpm. The back side design wash rate is 137 gpm. The lower side of the trap out trays are washed intermittently at an average rate of 40 gpm. The flow of fresh water makeup to the mist eliminator wash tank is controlled to maintain a constant level in the thickener overflow tank.

Waste slurry overflows each reaction tank by gravity and is collected in a common sump before it is pumped to the FGD thickener. The thickener is 165 feet in diameter and has a capacity of 2,000,000 gallons. Thickened sludge is pumped to one of two horizontal vacuum filters for final dewatering. The filter cake is combined with fly ash and lime prior to landfilling. Filtrate from the vacuum filter is returned to the thickener. Reclaimed water from the thickener is collected in the thickener overflow tank and returned to the scrubbers for washing the mist eliminators, cooling the flue gas in the presaturator, and milling limestone.

The limestone preparation equipment consists of a single wet overflow type ball mill operating in closed circuit with five 6-inch diameter hydrocyclones. The ball mill was supplied by Kennedy Van Saun, and the cyclones were supplied by Krebs. The ball mill was designed for a throughput of 42 tons per hour with a product size of 70 percent passing 200 mesh.

DISCUSSION OF RESULTS

In December 1984 a short-term test program was conducted at Indianapolis Power and Light, Petersburg Generating Station, to characterize the Unit 3 FGD system. A follow-up trip was made to investigate the operation of the system while adipic acid was being added to the scrubbers in March and April. This section summarizes the more significant results of these two trips. Information presented includes:

- Measured gas flow rates around the FGD system at two loads and at three levels of bypass,
- Observed SO_2 removal efficiency of individual towers without adipic acid addition,

- The effect of reaction tank pH on limestone utilization,
- Mist eliminator system description and recommendations to improve system reliability,
- Results of the stack particulate emission characterization and the contribution of particulates to the opacity problem, and
- The effect of adipic acid addition on scrubber performance.

GAS FLOW RATE MEASUREMENTS

An important part of the Petersburg 3 FGD system characterization was documentation of the flue gas flow rate at various points around the system. Previous gas sampling results had indicated that the system was treating higher than design gas flow rates at full load conditions (530 MW). This was thought to contribute to the severe mist eliminator scaling problem and to the reentrainment of mist from the back of the mist eliminators and accumulation of solids in downstream ductwork. As much as 500 tons of solids had been removed at one time from the ductwork between the scrubbers and the stack. In addition, the reentrainment of slurry was suspected of contributing to the periodic stack opacity problems on Unit 3.

Figure 2 is an isometric diagram of the Unit 3 FGD system showing the sampling points for the gas flow characterization. During the 3-day visit in December, the total gas flow entering the FGD system was measured by traversing at a location just before the ID fans. The total gas volume rate through the four towers was measured by traversing the outlet ducts for each tower. In addition, both reheat fan flow rates were determined by traversing their individual ducts. Finally, the stack flow rate was measured to serve as a check on the other measurements. These measurements could then be compared to determine the volume of gas bypassed.

Figure 3 is a simplified diagram of the FGD system showing the results of the flow characterization with the unit at full load - 530 MW. The flow is presented in dry standard conditions for ease of interpretation.

Examination of the data reveals an interesting observation. The total gas flow entering the FGD system measured at the inlet to the ID fans was 1.20 million dscfm. The total gas flow leaving the system measured in the stack was 1.57 million dscfm. The combined reheat flow was measured at .36 million dscfm. Subtracting the reheat flows from the stack flow gives 1.21 million dscfm, which agrees well with the total measured inlet flow to the system of 1.20 million dscfm. Comparing these flows with the combined measured flows from the four towers reveals a significant difference, however. The total flow from the towers was measured to be 1.43 million dscfm. This is 17 percent higher than the amount measured entering or leaving the system. This suggests that there was gas recirculation occurring during the sampling. In other words the booster fan inlet control vanes may have been

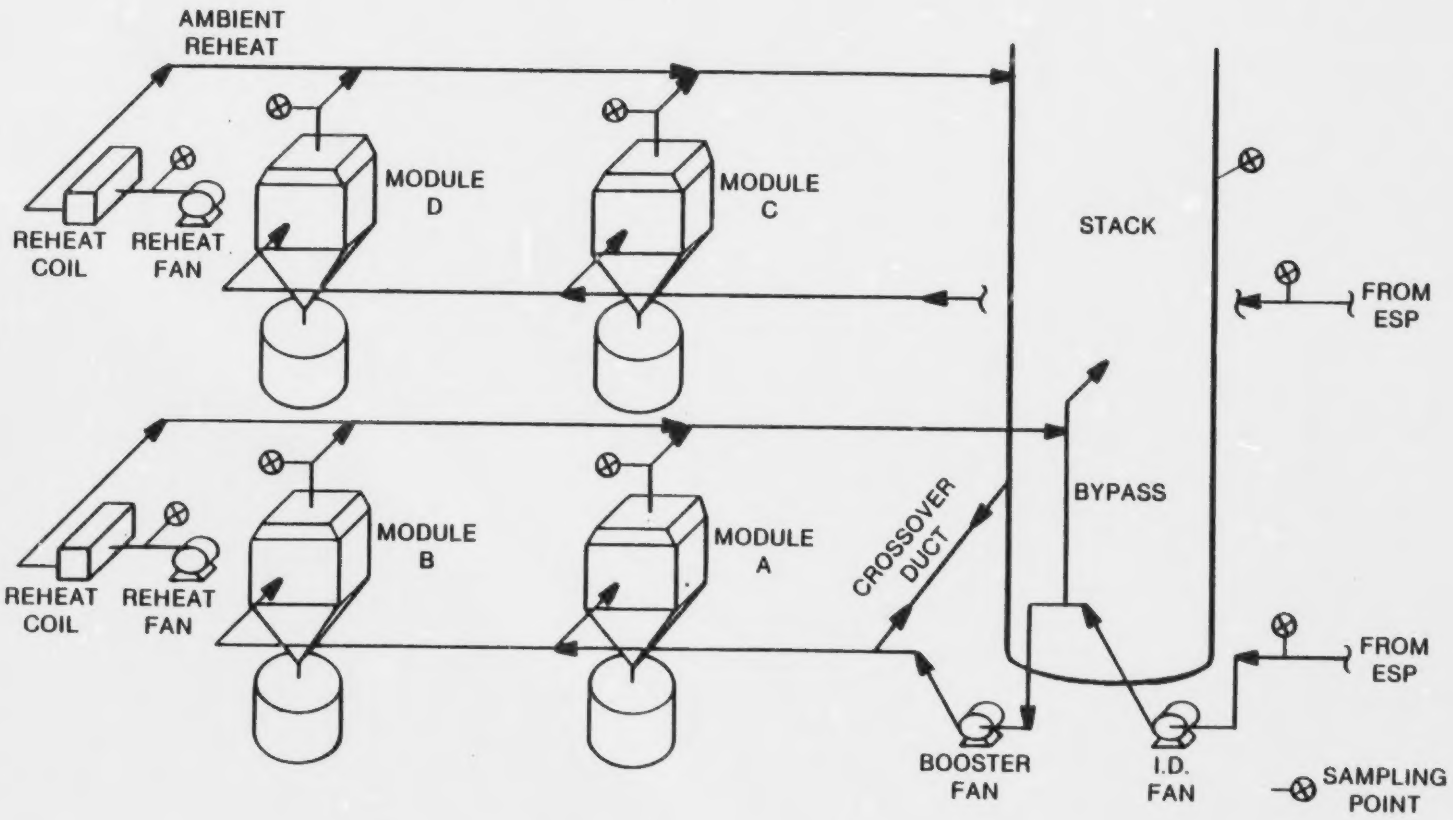

AMBIENT REHEAT
REHEAT COIL
REHEAT FAN
MODULE D
MODULE C
STACK
FROM ESP
REHEAT COIL
REHEAT FAN
MODULE B
MODULE A
CROSSOVER DUCT
BYPASS
FROM ESP
BOOSTER FAN
I.D. FAN
SAMPLING POINT

Figure 2. Isometric sketch of FGD system gas flow

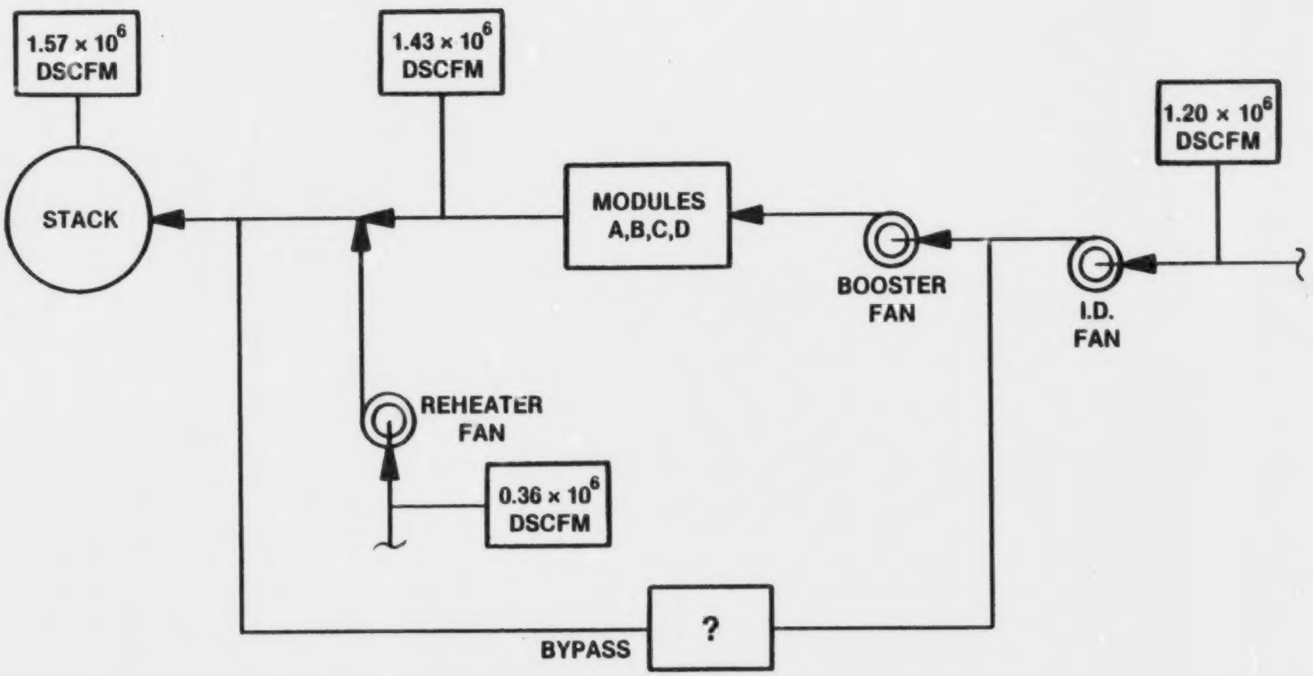

1.57 × 10^6 DSCFM
STACK
1.43 × 10^6 DSCFM
MODULES A,B,C,D
1.20 × 10^6 DSCFM
BOOSTER FAN
I.D. FAN
REHEATER FAN
0.36 × 10^6 DSCFM
BYPASS
?

Figure 3. Results of flue gas flow characterization.

opened too much and the fans were drawing gas back from the stack. A review of Figure 2 shows how this is possible. It is also possible that the error in the gas traverses caused this difference. To verify bypass or recirculation, it was recommended that sample parts be installed in the bypass duct. IPL has recently completed this modification.

The utility has reported problems in the past with recirculation of stack gas back through the booster fans. This situation has occasionally led to failure of the booster fans due to solids buildup on the fan impeller. The solids come from the mist which is reentrained from the backside of partially plugged mist eliminators. The booster fan inlet vane was set at 70 percent open during the testing. By closing the vanes the recirculation can be stopped. However, reducing the vane opening too much can cause excessive bypass of flue gas resulting in exceedance of the SO_2 standard.

Additional flue gas flow rate measurements were made with the booster fan vanes at different openings to determine the effect on the quantity of flue gas treated by the towers. Figure 4 presents the results of this work. Flow rate measurements were made with the unit operating at 460 MW and at 530 MW. The vane opening was varied from 55 percent to 70 percent. Results indicate that above a vane setting of about 55 percent, the towers are treating greater than design flows at 530 MW (390,000 acfm per tower). For the lower load of 460 MW, a vane opening of above 57 percent will result in greater than design flows. After the scheduled outage in May 1985, further testing is planned to verify the flue gas flow in the bypass duct. That vane opening which results in recirculation will be determined so that more accurate vane opening limits can be established.

SO_2 REMOVAL

During the 3-day December visit, the scrubbers were operated without organic buffer addition. The objective was to measure the performance of the FGD system without the presence of an SO_2 removal enhancement additive in the scrubbing liquor. The SO_2 concentration in the gas exiting each tower was determined at two loads and over a range of reaction tank pH's. SO_2 measurements were made by traversing the outlet ducts through sample ports installed by the utility just prior to testing. Traverses were used for the gas phase SO_2 measurements to eliminate the inaccuracies of spatial stratification of SO_2.

Figure 5 presents the results of the SO_2 measurements made at 460 MW and 530 MW for the four towers. The SO_2 concentration in each tower outlet is plotted against average reaction tank pH measured during the SO_2 traverse. The data show that pH has a strong effect on the removal efficiency of each tower. The data suggest that under prevailing conditions of coal sulfur, boiler excess air, and recycle pump performance the scrubbers should be operated at a pH of about 5.8 to achieve compliance, and if some bypass were desired, the scrubbers would have to be controlled at a pH of at least 6.2. As will be pointed out in the following section on Limestone Utilization, operation at pH 5.8 or higher is not recommended due to low limestone utilization and the potential increase in mist eliminator scaling rate.

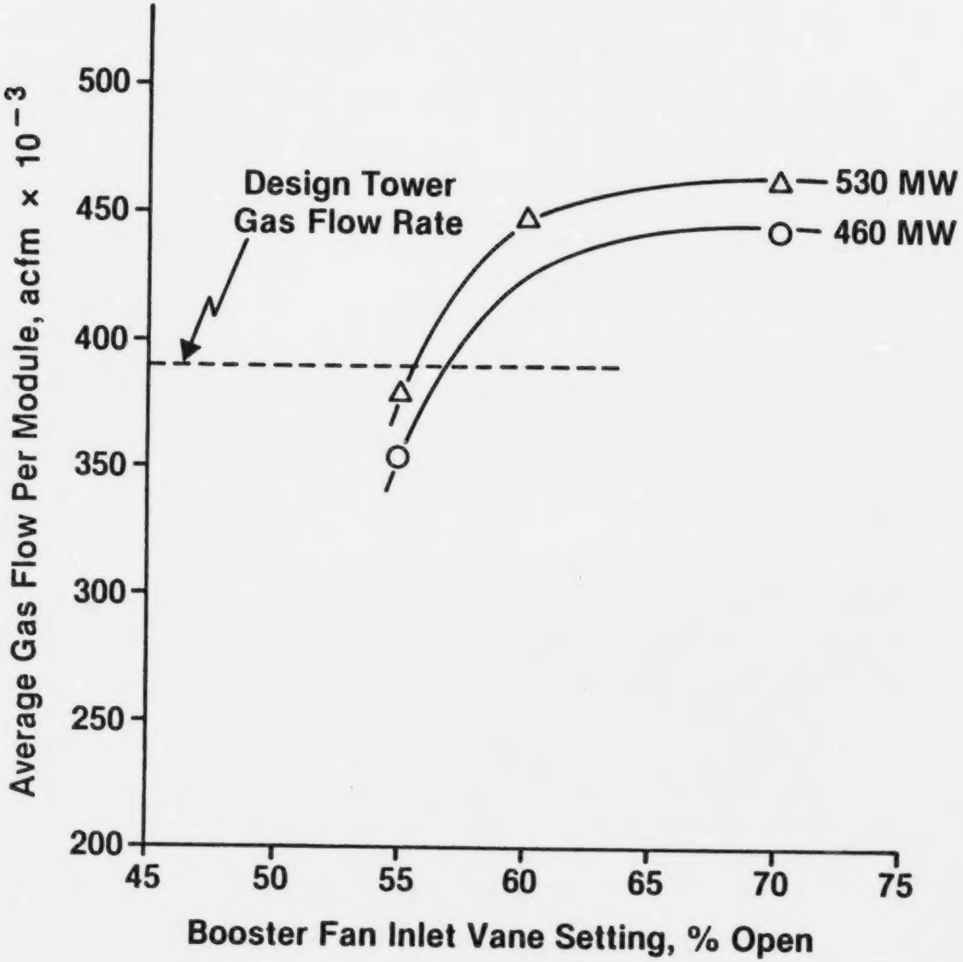


Figure 4. Effect of booster fan vane opening and unit load on tower gas flow rates.

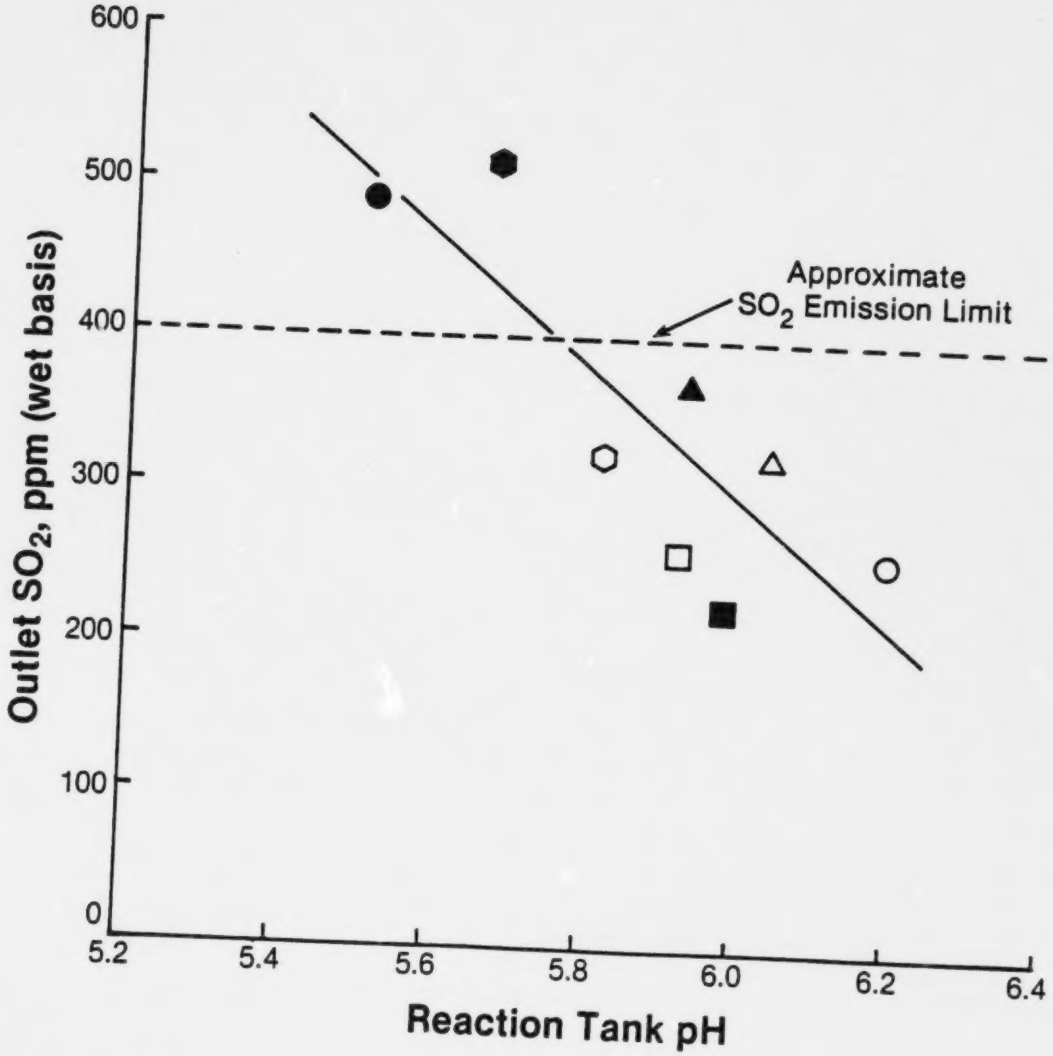


Figure 5. Effect of reaction tank pH on tower outlet SO_2 concentrations.

This analysis suggests that using an SO_2 removal enhancement additive such as organic buffer would be attractive in that simultaneous improvement in both SO_2 removal and limestone utilization would be possible. IPL has demonstrated improved SO_2 removal with the addition of organic buffers during earlier testing and plans to continue using the buffers in the future. The final section discusses the results of adipic acid testing conducted in March 1985.

Another point of interest in Figure 5 is the lack of any obvious effect of unit load on SO_2 removal efficiency. This results from the minimal decrease in the amount of gas treated by the towers in dropping the load from 530 MW to 460 MW. The booster fan vane opening was 70 percent for both tests. At the lower load the booster fans may have been recirculating more flue gas around the scrubbers. The measured drop in gas flow was only 5 percent for a 13 percent drop in unit load. Sulfur content of the coal burned during the SO_2 testing ranged from 2.7 to 2.9 percent.

LIMESTONE UTILIZATION

A number of slurry samples from the four scrubber reaction tanks were collected to measure limestone utilization. As each sample was collected, the pH of the slurry was measured with a portable meter. In addition, limestone slurry samples were collected periodically to measure the particle size of the limestone being fed to the reaction tanks.

Figure 6 presents the observed correlation between reaction tank pH and limestone utilization. The figure shows that pH had a definite effect on utilization, but that the normally sharp decline in utilization above a pH of 6.0 seen at most other limestone scrubbers was not seen at Petersburg. This might be explained by the relatively high concentration of magnesium carbonate (approximately 5%) in the raw limestone. A similar, almost linear relationship between pH and utilization was seen at another limestone scrubber which was tested with a limestone containing dolomite.

The relationship observed between pH and utilization can be used to select the proper operating setpoint for reaction tank pH. To ensure that a minimum of unreacted limestone is present in the reaction slurry, a pH setpoint of 5.6 is recommended. This will reduce the quantity of limestone carried up to the mist eliminators and therefore lower the amount of secondary scrubbing that will occur on the mist eliminators which leads to gypsum scaling. Operating at a pH that would allow adequate SO_2 removal (6.0 to 6.4) without using an SO_2 removal enhancement additive would result in fairly low utilizations of 75 to 80 percent. Operation at pH 6.2 to 6.4 was typical prior to organic buffer testing in the summer of 1984. Therefore, at the recommended setpoint of 5.6, some organic buffer addition will probably be required to achieve desired levels of SO_2 removal and bypass.

Samples of the limestone slurry fed to the scrubbers during utilization testing were collected for particle size analysis. The limestone averaged about 83 percent passing a 325 mesh screen (45 micron openings). Because of the effect of limestone particle size on reagent reactivity, the limestone

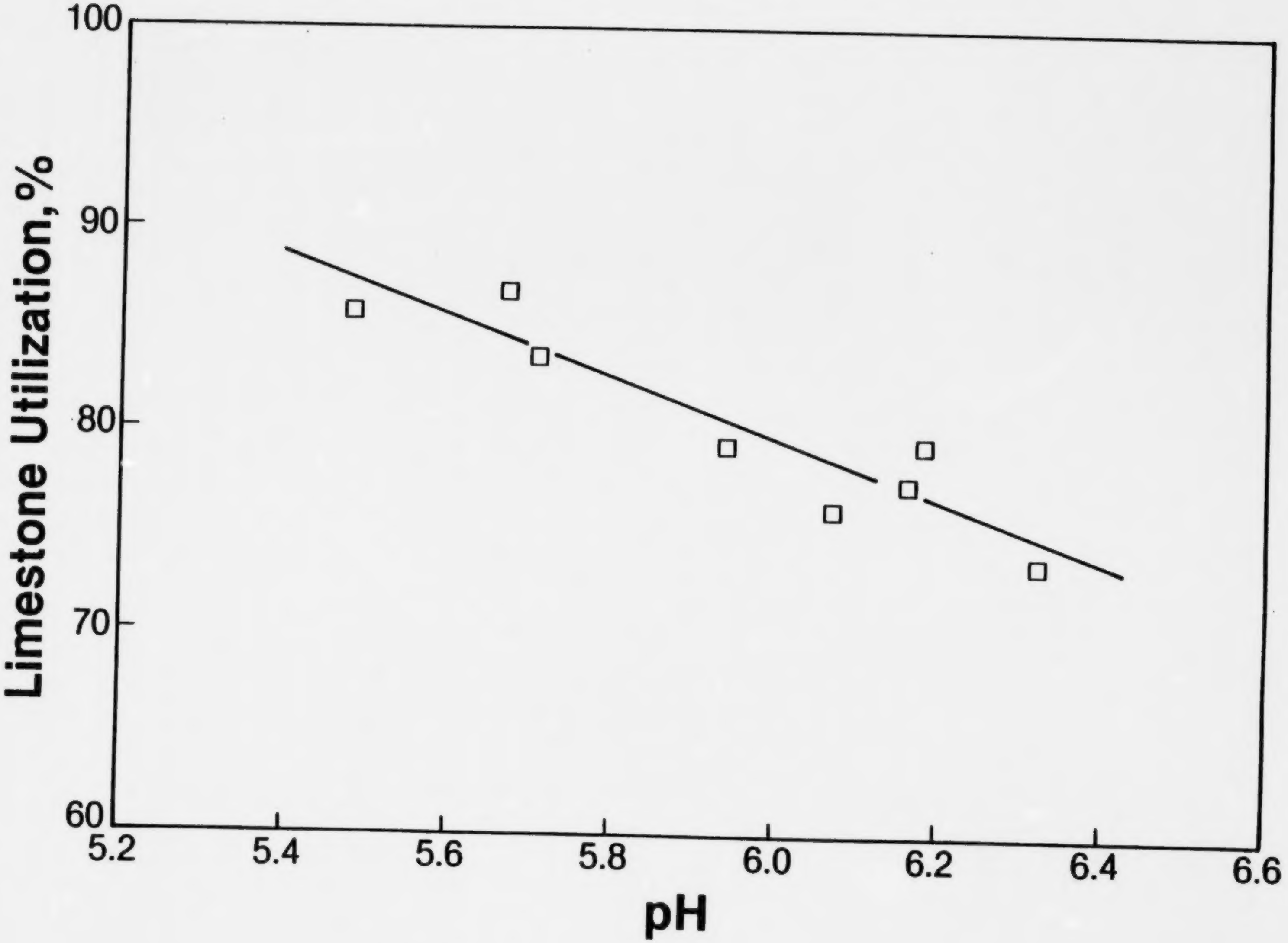


Figure 6. Observed relationship between scrubber pH and limestone utilization.

grinding circuit was studied to evaluate its performance and to determine the potential to upgrade its operation to produce a finer product size.

The limestone grinding circuit consists of a single KVS ball mill operating in closed circuit with five six-inch diameter Krebs classifiers. The design throughput of the system is 42 tons per hour for a limestone with a Bond Work Index of 10. The design product particle size specification is 70 percent passing a 200 mesh screen. IPL derated the mill circuit to produce a finer and more reactive limestone. The target particle size was 90 to 95 percent passing a 325 mesh screen.

A review of the circuit operation revealed that the mill was fed anywhere from 16 to 26 tons per hour of limestone with the lower tonnage being more common. The limestone had a top size of 3/4 inch and a Bond Work Index of about 11, which is a fairly hard stone. Also, only mill water was added to the circuit during operation. No dilution water was added to the mill product tank for dilution prior to the mill product being pumped to the classifiers. The classifiers had relatively small diameter apex and vortex finder sizes which should promote good separation.

Based on the review of the circuit, one change should yield a more consistent product particle size. It is recommended that dilution water be added to the mill product and the dilution water flow be controlled by feedback from the density meter which monitors the density of the slurry fed to the classifiers.

Figure 7 shows the results of measurements of the mill circuit performance operating without density control in March and April. The figure displays the strong influence that classifier product density has on the separation efficiency of the classifiers. The results show that by the addition of sufficient dilution water so that the circuit product density is 28 percent solids, a product particle size of almost 95 percent less than 325 mesh can be produced. With no other differences in mill circuit operation, a product of only 77 percent less than 325 mesh results with a more dense product of 37 percent solids.

MIST ELIMINATOR WASH SYSTEM

Figure 8 is a sketch of the upper part of the Petersburg 3 scrubbers showing the layout of the mist eliminators and trap out trays and their location relative to the upper sieve tray and slurry recycle headers. The purpose of the trap out trays is to catch most of the mist eliminator wash and segregate it from the slurry recycle loop by removing it from the tower and previously returning it to the mist eliminator wash tank. A portion of the trap out tray return was sent to the thickener. This limited the amount of solids sent back to the wash tank and subsequently to the wash nozzles.

Figure 9 presents a simplified diagram of the overall mist eliminator wash system and the approximate wash water flows at the time of the December visit. About 2300 gpm (estimated by the utility) of wash water was used with the lower mist eliminator being washed continuously and the trap out

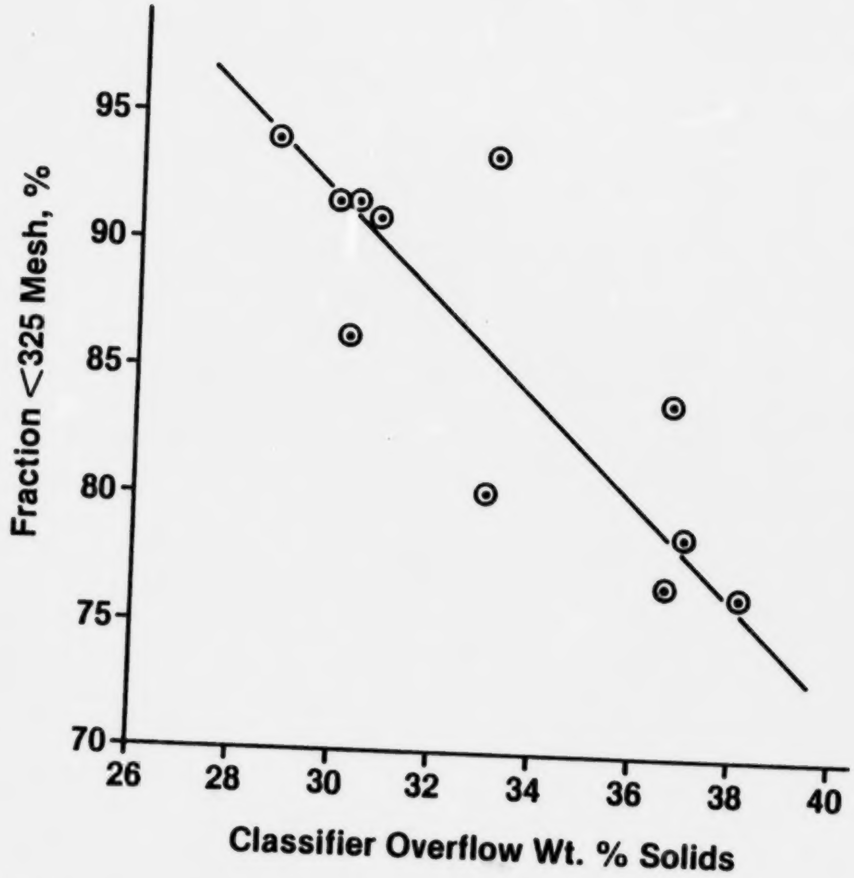


Figure 7. Effect of classifier overflow density on circuit product particle size.

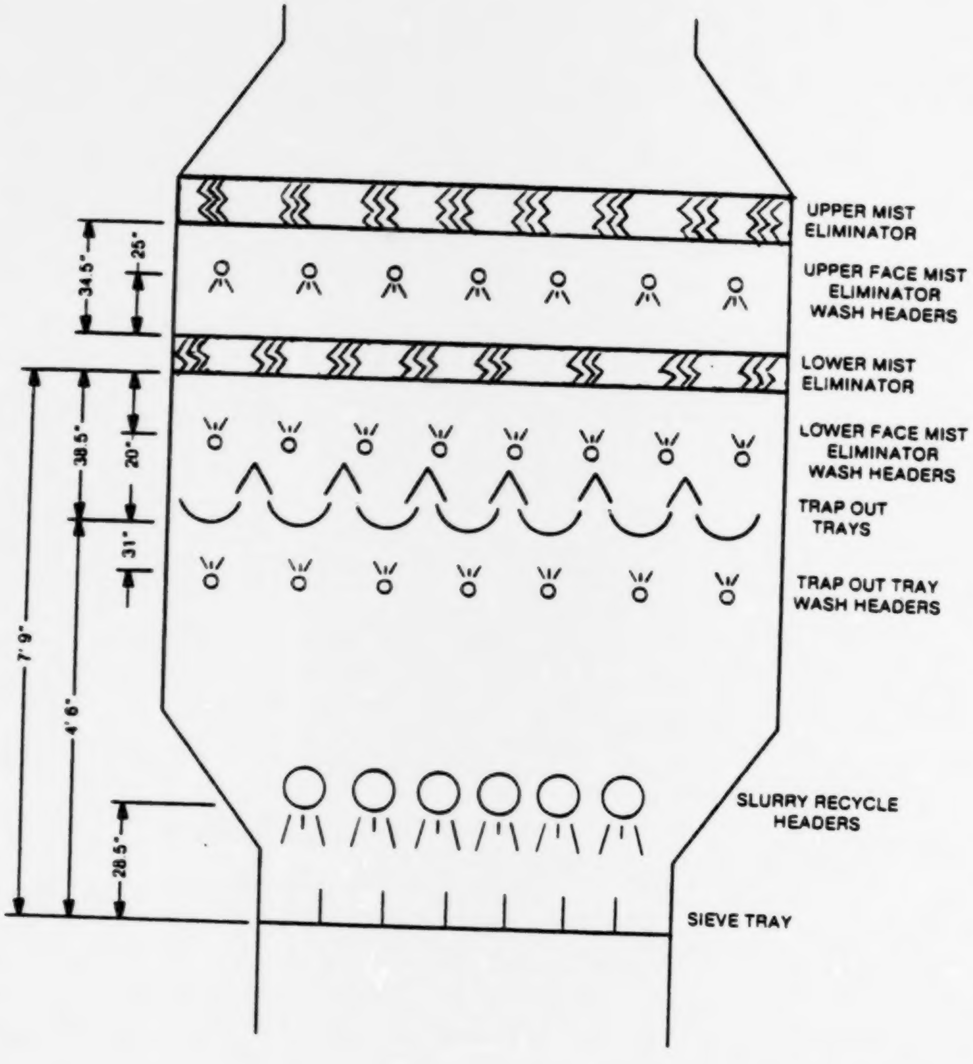

UPPER MIST ELIMINATOR
UPPER FACE MIST ELIMINATOR WASH HEADERS
LOWER MIST ELIMINATOR
LOWER FACE MIST ELIMINATOR WASH HEADERS
TRAP OUT TRAYS
TRAP OUT TRAY WASH HEADERS
SLURRY RECYCLE HEADERS
SIEVE TRAY
34.5"
25"
38.5"
20"
31"
7' 9"
4' 6"
28.5"

Figure 8. Dimensions of Petersburg 3 scrubber mist eliminator section.

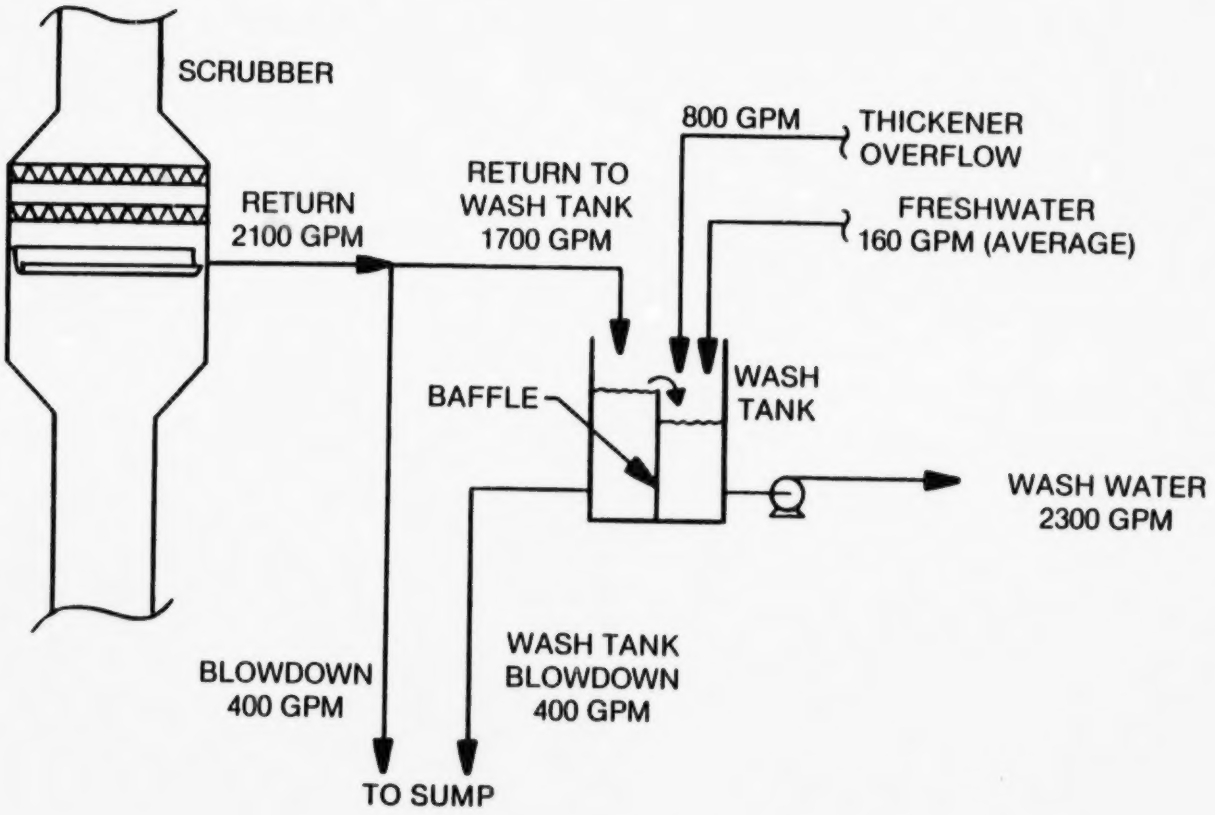

SCRUBBER
RETURN
2100 GPM
RETURN TO
WASH TANK
1700 GPM
800 GPM
THICKENER
OVERFLOW
FRESHWATER
160 GPM (AVERAGE)
BAFFLE
WASH
TANK
WASH WATER
2300 GPM
BLOWDOWN
400 GPM
WASH TANK
BLOWDOWN
400 GPM
TO SUMP

Figure 9. Previous mist eliminator wash scheme.

trays being washed intermittently. The lower face of the lower mist eliminator was washed at a specific wash rate of about 0.5 gpm/ft^2. The upper face was washed at a specific wash rate of about 0.25 gpm/ft^2.

During the December visit, samples of the mist eliminator wash were collected and analyzed along with samples of the mist eliminator wash return from the trap out trays (TOT). Results of analyses of major cations and anions in each of these streams were input to the Radian FGD liquid equilibrium model to predict the scaling potential (gypsum relative saturation) of the streams. The relative saturation of gypsum was strongly influenced by the addition of makeup water to the wash tank. Makeup water was added intermittently when the level in the thickener overflow tank dropped. When fresh water was not being added to the tank, the relative saturation of gypsum in the wash water was about 1.5. When fresh water is being added to the tank, the relative saturation dropped to 1.05. The relative saturation of the wash return was about 1.0 when fresh water was being added to the tank. No samples of the return were collected when fresh water was not being added due to time constraints. It is expected through, that a relative saturation of about 1.5 would have been seen in the return water without fresh water being fed to the tank.

This poor quality water is probably one of the causes of the scaling seen in the mist eliminator wash water. A modified wash scheme relying entirely on fresh water was recommended to IPL. This system has been recently installed (May) and is currently being used. The specific wash rate for the lower face of the lower mist eliminator is being increased to 1.5 gpm/ft^2 and the specific rate for the upper face of the lower mist eliminator is being increased to .55 gpm/ft^2 by replacing the nozzles. A timer was installed so that wash frequency could be controlled to prevent excess quantities of fresh water from entering the FGD system and upsetting the water balance. The wash frequencies and specific wash rates chosen are based on the results of work performed at the EPA Alkali Scrubbing Test Facility - Shawnee(1).

The installation and evaluation of at least three mechanical seals for the slurry recycle pumps is planned. The purpose is to study the ability of the seals to reduce the fresh water consumption by the scrubbers to allow additional water for use in washing the mist eliminators or to help prevent discharge of water from the system due to a positive balance.

STACK PARTICULATE EMISSIONS CHARACTERIZATION

Measurements were made in the Unit 3 stack during the December testing to attempt to determine the cause of the plant's periodic opacity problem. The following measurements and analyses were made:

- particulate mass concentration,
- particle size distribution, and
- chemical analysis of the particulate matter.

All runs were made with the unit operating at full load (530 MW). Mass loadings and particle size distribution were measured using a single point location in the stack. Particulate samples were analyzed for trace elements by X-ray fluorescence (XRF) and for major elements by inductively coupled plasma emission spectroscopy and XRF. Although the mass emissions sampling were intended only for chemical characterization, they were used as a measure of mass loading. The average mass emission rate for the tests was 0.09 lbs/MMBtu. The mass emission standard is 0.10 lbs/MMBtu for Petersburg 3. Thus the opacity does not appear to be qualitatively related to an excess mass emission level. A more thorough set of mass emission testing is planned.

The particle size distribution of the stack particulate emissions is shown in Figure 10. The data are presented as a differential particle size versus particle diameter. The particle size distribution shows two distinct modes with mean diameters of 0.25 microns and nominally 10 microns. These fractions account for 75 percent and 25 percent of the total mass concentration, respectively. Because of the unit's periodic high opacity readings, an attempt was made to determine the potential opacity of the stack particulate emissions. No transmissometer exists at the stack location, and weather conditions made it impossible to visually determine the opacity of the stack emissions (EPA Method 9). Therefore, the particle size data were used to calculate the light extinction coefficient distribution. Extinction coefficients were calculated for discrete particle size intervals (physical diameters, assuming a density of 2.5 gms/cc for fly ash and 1.8 gms/cc for H_2SO_4 mist) using light extinction efficiency factors for a refractive index of 1.5 and a wavelength of 550 nm (van de Hulst, 1957). The extinction distribution is presented as a differential plot for aerodynamic particle size to allow direct comparison to the particle size distribution. The total area under the curve represents the total extinction. The total extinction is used to calculate the stack opacity using the Beer-Lambert law (optical pathlength equal to the stack diameter). These calculations indicate that opacities in excess of 50% are possible for the stack particluate emissions. The distribution function shows that the high opacity results almost entirely (95%) from the submicron fraction. This suggests that reported opacity problem may be related H_2SO_4 mist concentrations in the flue gas.

Information about the particulate matter composition was obtained by a variety of techniques. Filter catches from the mass testing were examined with a scanning electron microscope/microprobe in an attempt to identify the presence of flyash, scrubber related solids and condensed H_2SO_4 mist. Sulfur was the predominate element in the solids. No other elements were present in sufficient quantify to be combined with the sulfur, thus suggesting that it was the H_2SO_4. A portion of the mass loading particulate filter, plus the final stage and final filter of the size distribution measurements were leached in a small quantity of water and the pH of the resulting solution was determined. In all cases the pH was less than 2, indicating the presence of an acid.

From this information, the material observed appears to be mainly H_2SO_4. Since H_2SO_4 is expected to be present in the stack gas as a submicron mist particle it probably is the major contributor to the mass observed

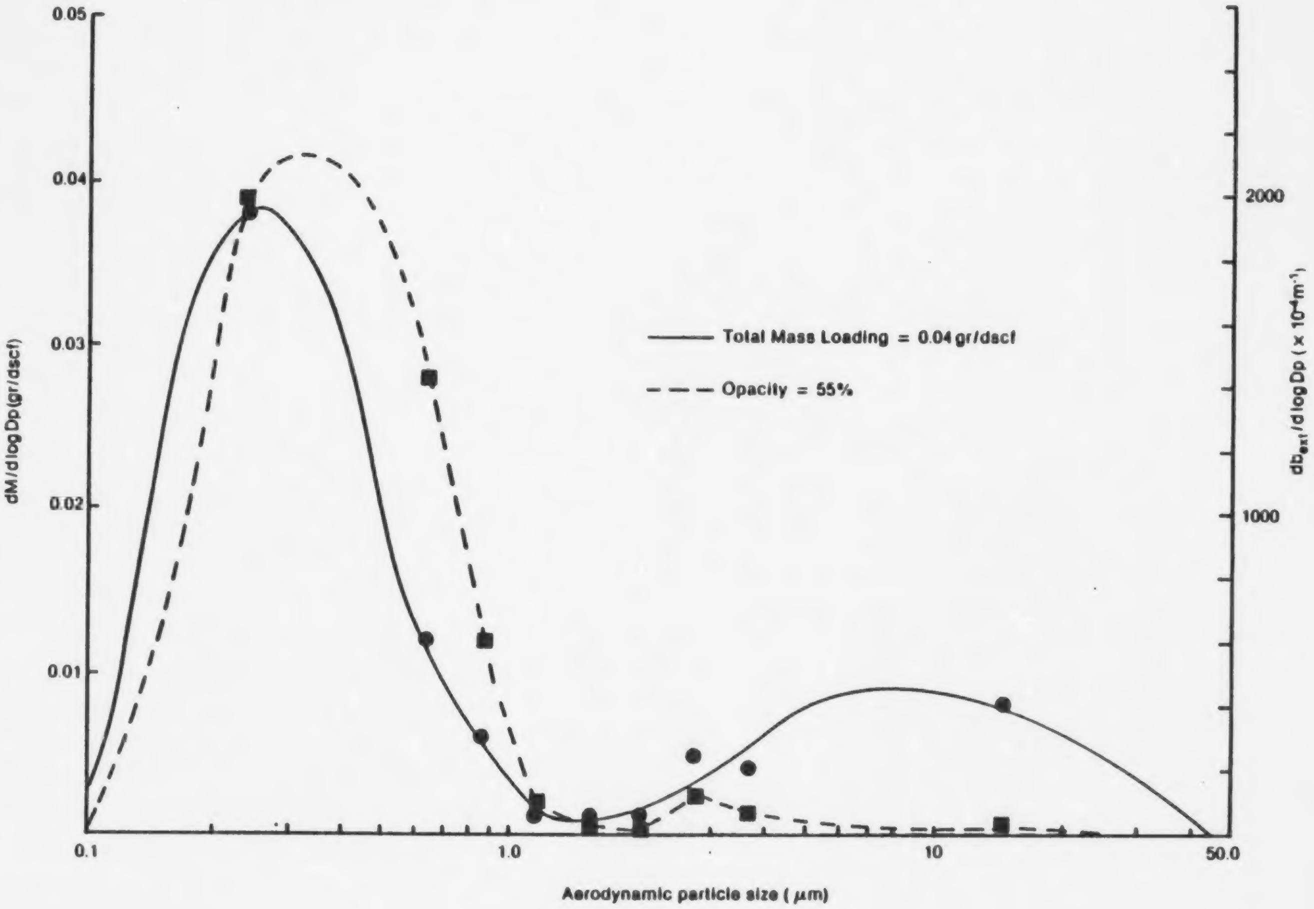


Figure 10. Differential particle size distribution for mass concentration and light extinction coefficient.

in that size range. The analytical results also indicate that the only other significant material in the particulate matter is fly ash.

ADIPIC ACID TESTING

Adipic acid testing was conducted during a three week period in March 1985 to determine the consumption rate of adipic acid. Essentially pure adipic acid in the powder form was introduced to the FGD system with the limestone slurry. The feed rate varied between 750 and 900 lb/day, with one-third of the daily total added once per shift. The addition rate was controlled to maximize the bypass of flue gas with a reaction tank pH setpoint of 5.6. The average tower removal efficiency was about 95 percent during the period.

Adipic concentrations in the system were monitored by periodically collecting and analyzing samples from the four reaction tanks, the thickener overflow and the limestone slurry storage tanks. Results from the analyses were used to track adipic concentrations and to calculate initial and final inventories of adipic acid in the FGD system. The total adipic acid feed and the initial and final inventories were used to calculate adipic consumption. Coal sulfur content and heat content, Unit 3 load and heat rate, and stack outlet SO_2 and CO_2 were used to determine the amount of SO_2 removed during the test. This allowed normalization of the adipic consumption rate in terms of pounds of additive consumed per ton of SO_2 removed.

The average adipic acid concentrations are presented in Table 1 along with the average weight percent solids. The adipic concentrations did not fluctuate widely in the individual modules. However, the concentrations did vary considerably between scrubber modules due to significant differences between liquid residence times in the modules. Modules A and B operated at low suspended solids levels, which results in short reaction tank residence times. Low adipic acid concentrations resulted. High weight percent solids in Modules C and D indicated longer residence times and, therefore, higher adipic acid concentrations.

Average operating conditions during the test period are presented in Table 2. The SO_2 emissions were below the 1.20 lb/MMBtu limit. The coal sulfur content averaged 2.1 percent. The load averaged 414 MW over the period. The unit operated with a general 50 MW derate to help prevent mist eliminator scaling by reducing the amount of gas sent through the towers and to prevent flue gas recirculation. Over the period, the mist eliminator scaling rate was significantly reduced. Therefore, the combination of boiler derating, maximum bypass, and good limestone utilization was effective in preventing scale formation in the mist eliminators.

The adipic acid consumption rate over the test period was 6.5 lb adipic acid per ton of SO_2 removed. The theoretical consumption rate, defined as the amount of adipic acid lost with water in the filter cake, was 3.0 lb adipic acid per ton of SO_2 removed, resulting in an actual-to-theoretical consumption rate of approximately 2.2. These numbers were surprisingly low. This consumption rate was less than one-third the observed rate at City Utilities Southwest Power Plant for equivalent reaction tank concentrations.

TABLE 1. AVERAGE ADIPIC CONCENTRATIONS AND SOLIDS CONTENT

	Adipic Acid Concentration		Weight Percent Solids	
	Average ppm	Standard Dev. ppm	Average %	Standard Dev. %
Module A	1080	120	5.4	0.7
Module B	990	100	4.2	1.0
Module C	1500	180	8.6	0.8
Module D	1610	240	9.9	1.1
Thickener Overflow	820	80	-	-
Limestone Slurry	1650	160	30.4	1.8

TABLE 2. OPERATING CONDITIONS DURING ADIPIC ACID TESTING

	Average	Standard Deviation
Coal		
Sulfur Content, %	2.08	0.28
Heat Value, Btu/lb	12,098	204
Unit 3 Boiler		
Load, MW	414	67
Heat Rate, Btu/kWh	10,400	120
SO_2 Emissions, lb/MMBtu	1.06	0.09

Compared to the results at San Miguel, the rate is about one fifth of that measured during the testing there for similar reaction tank concentrations.

Analysis of solid samples collected from the reaction tanks indicated an average oxidation of approximately 18 percent, which is close to the 20 percent oxidation measured during testing without adipic acid. The limestone utilization during testing with and without adipic acid is presented in Figure 11. There is no apparent effect of adipic acid on limestone utilization.

REFERENCES

1. EPA Alkali Scrubbing Test Facility: Advanced Program, Second Progress Report, Head, Harlan H., et al, Sept. 1976. EPA-600/7-76-008.

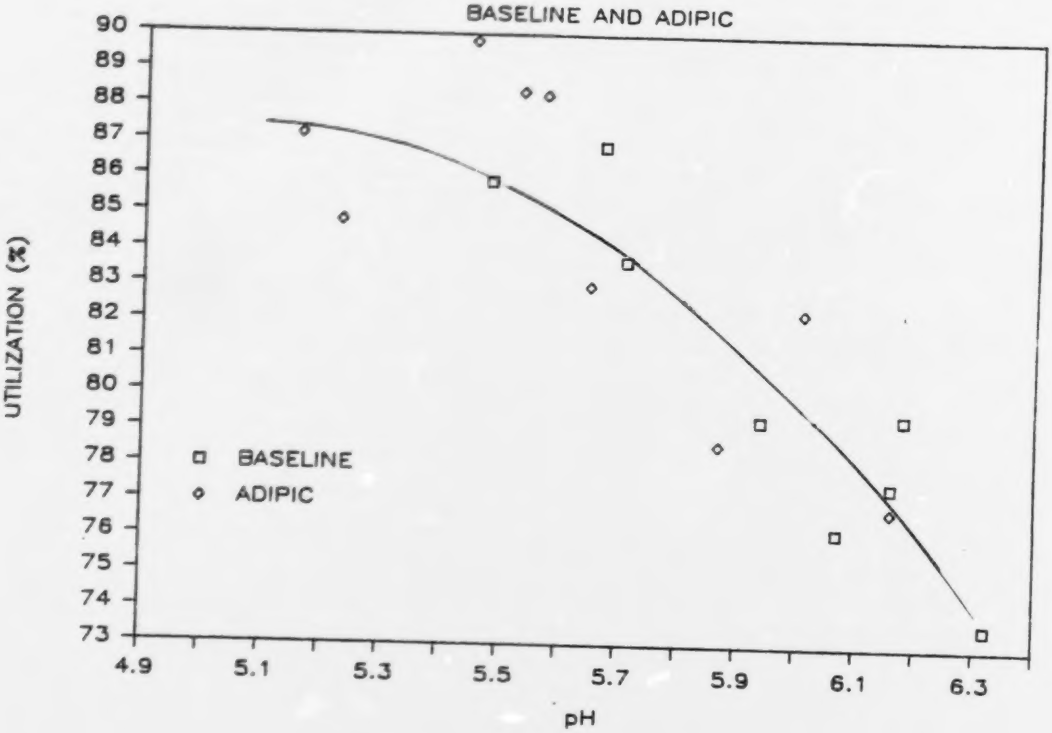


Figure 11. Limestone utilization.

RESULTS OF AN FGD PROCESS TROUBLESHOOTING PROGRAM AT TEXAS UTILITIES, MARTIN LAKE STEAM ELECTRIC STATION

By: David Colley
Radian Corporation
Austin, Texas 78758

Don Mzyk
Texas Utilities Generating Co.
Martin Lake Station
Tatum, Texas 75691

Mike Wadlington
Texas Utilities Generating Co.
Dallas, Texas 75201

Dorothy Stewart
Electric Power Research Institute
Palo Alto, California 94303

ABSTRACT

The objectives of the troubleshooting program at the Martin Lake Station were to reduce the operating and maintenance costs and to improve reliability of the limestone FGD system. The problem areas addressed include chemical scaling in the absorber packing and mist eliminators, process control and instrumentation, system water balance, and limestone utilization. The troubleshooting methodology used to solve the problems is outlined. A three-month demonstration test was undertaken to verify the success of recommended process changes to reduce gypsum scale formation rates and to improve process stability. The results of the demonstration testing showed that scale formation in the absorber packing and mist eliminator could be virtually eliminated. Recommendations to convert the FGD system from a water producer to a water consumer are listed. Also, recommendations to increase limestone utilization are presented.

INTRODUCTION

The results of a year-long program to improve the reliability of the Texas Utilities Generating Company (TUGCo) Martin Lake FGD system are presented in this report. The program was funded by the Electric Power Research Institute as a part of a research project (RP-2248-1), to define and solve chemical process problems in wet FGD systems. The program at Martin Lake was begun March, 1983, and was completed in June, 1984.

The Martin Lake Steam Electric Station is a base loaded, mine-mouth generating plant located near Tatum, Texas. The station consists of three 770 MW units which fire a lignite fuel. Unit 1 began commercial operation in 1977, with Units 2 and 3 beginning operation in 1978 and 1979 respectively. All three units are subject to the 1971 EPA New Source Performance Standards for fossil fuel fired utility boilers. The sulfur dioxide emissions are controlled with a limestone scrubbing system supplied by Research-Cottrell.

PROGRAM BACKGROUND

Since startup, the reliability of the FGD system has been limited by pluggage of the primary packing and mist eliminators in the scrubbers with gypsum scale. TUGCo was using a crew of about 80 men to service its 24 scrubber towers at the rate of 2 to 3 towers per week. TUGCo had been addressing the problem of gypsum scaling in the tower wetted film contractor for several years prior to this program. Due to the "domino" effect of several mechanical problems, along with the process chemical problems, the resolution had not come as fast as it was needed. In the Spring of 1982, TUGCo enlisted the services of an independent FGD consultant to review the current status of their scrubbers and to identify a course of action that would lead to the resolution of the chemical problems that had been hindering their operation.

As the consultant′s review was being completed in September of 1982, TUGCo formed a task force to act on the various recommendations received to that date on courses of action to improve the operation of the scrubber system. This task force was composed of representatives from the plant, the corporate engineering group and technical support group, the FGD system′s original equipment manufacturer (O.E.M.) and the independent consultant. Coincidental to this review process, TUGCo was invited by EPRI to participate in the FGD Chemical Process Program in mid-November of 1982, and on January 3, 1983, accepted the invitation.

A brief chemical and process characterization of the FGD system was performed by Radian, EPRI′s contractor on the Martin Lake project, in March, 1983, to collect information that would be useful in identifying the cause of the scale formation in the towers. The results of this work are presented in the report. This, along with the results of previous testing done by TUGCo and the O.E.M., were reviewed and potential solutions to scaling were identified. A program, based on EPRI′s independent evaluation of previous TUGCo work and their own testing, was recommended to the utility to demonstrate the effectiveness of proposed equipment and operational changes to reduce or eliminate the scale formation in the towers. After review by the utility's FGD Task Force, the recommendations were incorporated on four towers on Unit 3 for testing and evaluation.

The testing and evaluation phase began in December, 1983, and extended through April, 1984. The changes made on two of the towers were successful in stopping the scale formation in the tower packing over a three-month period. Use of higher mist eliminator wash rates in conjunction with the changes to stop scaling in the packing succeeded in stopping the mist eliminator scaling as well. In addition to the work on the scale formation problem, a new, more durable primary packing was tested to qualify it as a replacement for the existing, more fragile design.

The FGD system operated with a positive water balance that required the installation and operation of expensive water treatment equipment to control the large surplus of water generated daily by the scrubbers. A list of recommendations were made that would result in the FGD system being a net consumer of water. The effect of these changes on the current water balance is presented.

Finally, recommendations to improve the utilization of limestone in the scrubbers are made. Process setpoints for pH are recommended for each of the two recycle loops considering SO_2 removal efficiency, utilization, and forced oxidation.

FGD SYSTEM DESCRIPTION

The Martin Lake Steam Electric Station of Texas Utilities is a planned four 750 MW (net) unit plant. It is located approximately 120 miles east of Dallas, Texas, near the town of Tatum. Units 1, 2, and 3 are currently operating, and were started up in April, 1977; May, 1978; and February, 1979, respectively. Martin Lake Unit 4 is not scheduled for operation until after 1990. The fuel burned at Martin Lake is Texas lignite that is mined near the plant site. The lignite varies in sulfur content from 0.9 percent to 3.8 percent and in heating values from 6,000 Btu/lb to 7,200 Btu/lb. A cold side electrostatic precipitator supplied by Research-Cottrell is used to limit particulate emissions to below the 1971 NSPS regulation of 0.1 lbs/10^6 Btu. Information on the design and operation of the FGD system, also supplied by Research-Cottrell, is presented in the following sections.

SYSTEM GAS FLOW

Design gas flow at full unit load is 3,900,000 acfm at 360°F. At scrubber outlet conditions (140°F and saturated with water), this is equivalent to 3,100,000 acfm. Stack test results indicate that the volume averages 2,400,000 acfm at scrubber conditions, however. Depending upon the SO_2 content of the flue gas, the volume of gas treated will vary from about 75 percent of the total under low SO_2 conditions to 95 percent under high SO_2 conditions. The gas not treated is bypassed around the scrubbers for reheat purposes. Inlet SO_2 concentrations have been roughly correlated to lignite sulfur content according to the following equation:

$$\text{Inlet Gas } SO_2\text{, ppmv} = 900 \times S,$$

where S = percent sulfur in the lignite, dry basis.

Factors which affect this relationship include excess air, moisture, and lignite heating value. Figure 1 presents the relationship between total gas flow as measured by stack velocity traverses and unit load.

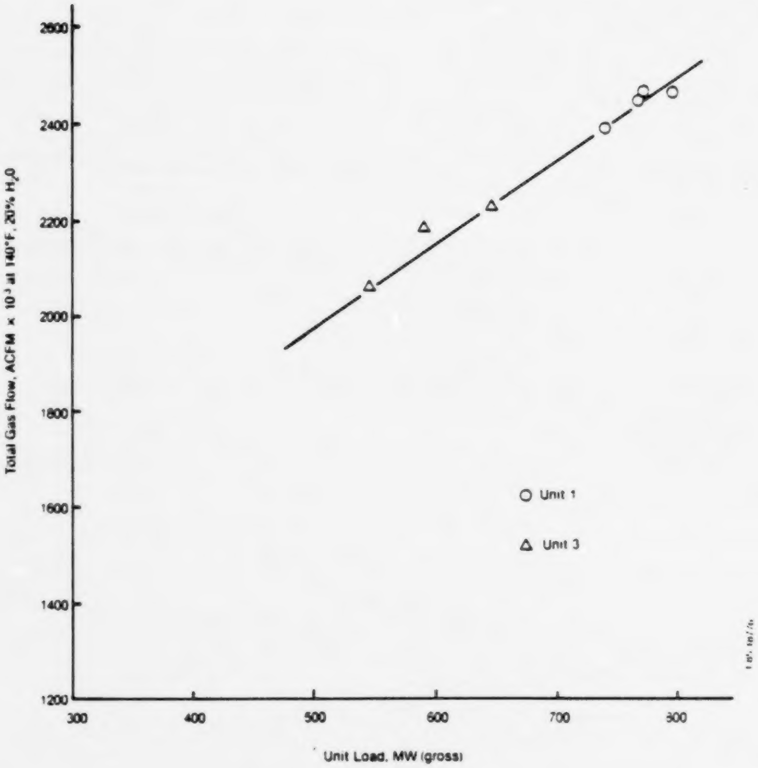


Figure 1. Gas Flow as a Function of Unit Load - Martin Lake Steam Electric Station.

Figure 2 is a simplified plan view of the Martin Lake station showing the layout of the FGD system. Each unit has eight towers which were supplied by Research-Cottrell. Six towers were originally installed with the units. At 28 feet in diameter, they were designed to each treat a maximum of 330,000 acfm, saturated at 140°F. Two additional towers were retrofitted in early 1983, to increase the gas treating capacity of each system so that a higher sulfur lignite could be burned in the boilers. These towers are 34 feet in diameter and each was designed to treat a maximum of 490,000 acfm at 140°F.

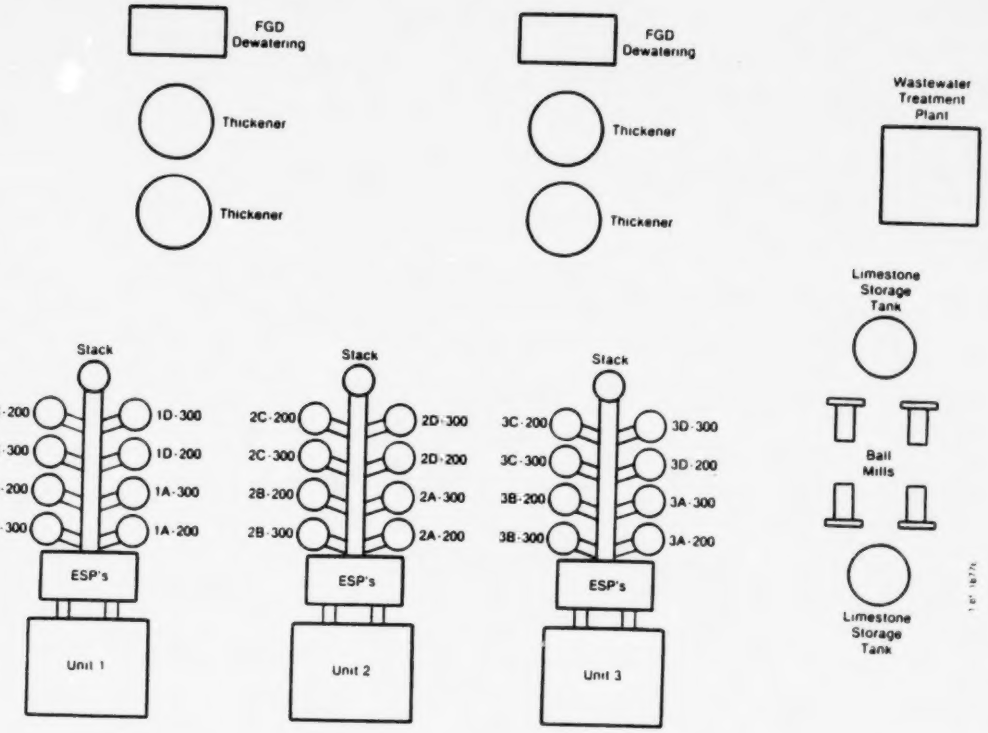

FGD Dewatering
Thickener
Thickener
FGD Dewatering
Thickener
Thickener
Wastewater Treatment Plant
Limestone Storage Tank
Stack
1C-200
1C-300
1B-200
1B-300
1D-300
1D-200
1A-300
1A-200
ESP's
Unit 1
Stack
2C-200
2C-300
2B-200
2B-300
2D-300
2D-200
2A-300
2A-200
ESP's
Unit 2
Stack
3C-200
3C-300
3B-200
3B-300
3D-300
3D-200
3A-300
3A-200
ESP's
Unit 3
Ball Mills
Limestone Storage Tank

Figure 2. Plan View of Martin Lake FGD System.

Figure 3 is a flow diagram of a single tower. The tower is a vertical Double Loop (Research-Cottrell trademark) wet limestone SO$_2$ scrubber. Flue gas enters tangentially at the bottom of the tower where it is cooled and saturated in a short spray tower section termed the quencher. Slurry is recycled at a rate of 7,800 gpm through the bank of spray headers in the quencher in the 28-foot diameter towers and at a rate of 9,400 gpm in the 34-foot diameter towers. This gives an L/G radio of 24 for the smaller towers and 19 for the larger towers at design gas flow rates. Each tower´s quencher was retrofitted with a forced oxidation sparger capable of producing a high quality gypsum by-product. Depending upon inlet SO$_2$ concentrations, recycle slurry, pH, gas flow rate, and slurry recycle rate, the quencher SO$_2$ removal efficiency varies from 20 percent to 50 percent of the inlet SO$_2$ loading, and averages about 30 percent.

From the quencher, the flue gas passes through a bowl-type separator which segregates the quencher slurry of lower recycle loop from the upper loop of the tower. The upper loop is designed to achieve most of the SO$_2$ removal. This loop consists of an initial spray section followed by a packed section. Table 1 presents the information on the design slurry recycle rates for the upper loops.

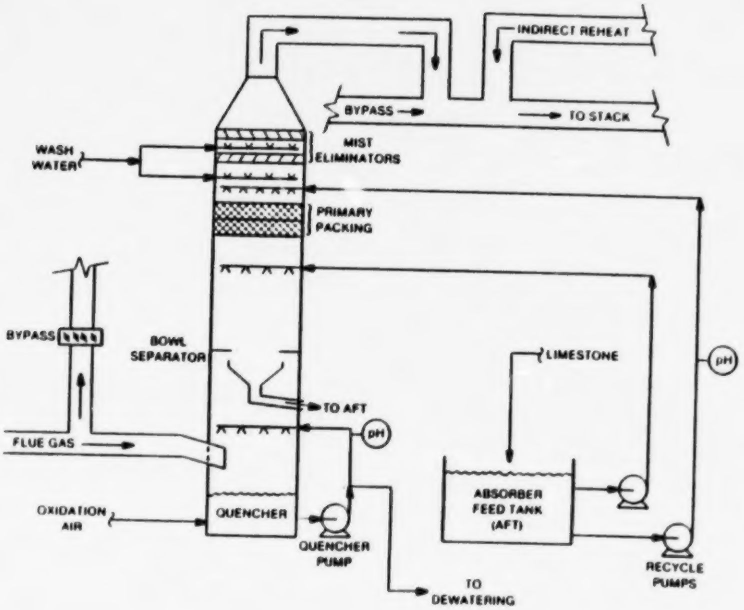

INDIRECT REHEAT
BYPASS
TO STACK
WASH WATER
MIST ELIMINATORS
PRIMARY PACKING
BYPASS
BOWL SEPARATOR
LIMESTONE
pH
TO AFT
FLUE GAS
pH
OXIDATION AIR
QUENCHER
ABSORBER FEED TANK (AFT)
QUENCHER PUMP
TO DEWATERING
RECYCLE PUMPS

Figure 3. Flow Diagram of Martin Lake Scrubber.

TABLE 1. UPPER LOOP RECYCLE RATES

Unit	Tower Diameter, ft	Recycle Rate, gpm	Design Gas Flow, ACFM*	Liquid-to-Gas Ratio, gals/10^3acf
1,2	28	22,900	330,000	69
3	28	29,800	330,000	60
1,2,3	34	34,340	490,000	70

*140°F, saturated.

The overall tower L/G′s are presented in Table 2.

TABLE 2. DESIGN TOWER L/G RATIOS

Unit	Tower Diameter, ft	Recycle Rate, gpm	Design Gas Flow, ACFM*	Liquid-to-Gas Ratio, gals/10^3acf
1,2	28	30,700	330,000	93
3	28	27,600	330,000	84
1,2,3	34	43,800	490,000	89

*140°F, 20% H_2O.

The spray section nozzles operate at a pressure of about 15 psi. The packed section of each tower consists of a two-foot deep section of a polypropylene wetted film contactor (called primary packing) designed to improve the gas-liquid contacting surface area within the tower to promote SO_2 removal. At design gas flows, the pressure drop across clean packing is approximately 0.5 inches of H_2O. Overall tower design pressure drop is 6 inches H_2O.

Two banks of mist eliminators are used in each tower to remove entrained slurry from the flue gas. The first bank is designed to remove only the larger diameter droplets. The second stage is designed to complete the mist capture. Both are based on a chevron type configuration. The lower side of each are washed periodically for cleaning. The wash water enters the upper loop and serves as a source of dilution water.

Each tower has its own quencher. However, the upper loop recycle tank or absorber feed tank (AFT) is common to two towers. Therefore, for each unit, there are eight quenchers and four AFT's. The volume of the 28-foot diameter tower quenchers is 34,400 gallons, and for the 34-foot diameter towers, it is 50,800 gallons. The AFT volume for the smaller towers is 268,000 gallons, and for the larger towers, it is 426,000 gallons.

Limestone slurry is added to the AFT's to maintain a pH setpoint of 5.8. All slurry overflowing the AFT's is fed to the quenchers. Limestone reagent is now added directly to the quenchers. The density in the quenchers is controlled by discharging slurry to the thickeners on high density. The level in the quencher tanks is controlled by returning thickener overflow to the tank.

SOLIDS DEWATERING

The quencher sump of each tower is equipped with an air sparger which injects forced oxidation air from a compressor station and yields a 90 percent or better oxidation rate. Oxidized slurry from the tower quenchers is discharged directly to solids dewatering. A thickener provides the initial solids separation step. The thickener overflow is returned to the quenchers as dilution water. A given unit's thickener underflow slurry is pumped to either of three centrifuges or one vacuum filter per unit for the final dewatering step. The dewatered sludge from the centrifuges at 65 to 70 wt. percent solids is mixed with fly ash to stabilize it and disposed of in a permitted disposal area. The sludge from the filter at 80 to 90 wt. percent solids is stable enough to be disposed of directly without further stabilization.

LIMESTONE REAGENT PREPARATION

Limestone is the alkaline reagent used to react with the SO_2 absorbed in the scrubbers. The limestone is delivered by rail from two plants located in Texas. The bulk of the material received is already a very fine particle size. This material is purchased from lime plants where it is undersize reject. The limestone is relatively soft, having a Bond Work Index of about 6.0.

The limestone is ground in one of four wet overflow type ball mills operating in closed circuit with hydrocyclones for particle size control. The mills are designed to process 60 tons per hour of limestone and produce a product of which 70 percent will pass a 200 mesh screen. The use of lower Bond Work Index limestone than design and less than maximum tons per hour thruput typically yields a finer grind than this design value. Product from the mill circuit is stored in one of two tanks prior to being fed to the FGD system. The product slurry is typically 35 to 40 percent solids.

WASTEWATER TREATMENT PLANT

The Martin Lake FGD system has historically operated with a positive balance. The purpose of the wastewater treatment plant is to process this water so that it may be recycled to the FGD system for use as mist eliminator wash water or pump seal water. The plant consists of a pretreatment system, a reverse osmosis unit, and a brine concentrator.

The pretreatment system is made up of a lamella thickener, a reactivator clarifier, sand anthracite filters, and chemical support systems. The purpose of the pretreatment system is to remove the calcium and magnesium hardness in the wastewater prior to feed to the reverse osmosis (RO) unit.

The reverse osmosis unit consists of micron cartridge filters, booster pumps, and two stages of RO elements. The brine concentrator is a large heat exchanger/vapor compression distillation unit. It is designed to operate without pretreatment of the wastewater, and it can process about 640 gpm of wastewater. Reject brine from the brine concentrator is disposed of by deep well injection. The brine generation rate is a function of the total dissolved salt content in the water fed to the brine concentrator. A typical brine blowdown rate for the Martin Lake unit is 30 gpm.

OPERATING HISTORY

The ability to pass boiler gases through the scrubber towers dictated, to a large extent, the ability to operate the MLSES units at maximum output and in compliance with SO_2 emission standards from mid-1979 to late 1981. Gas flow through a scrubber tower varied due to the uncontrollable pluggage of that tower's packing. By far, the most costly problem with Martin Lake's scrubber towers, in terms of both maintenance expense and loss of generation due to compliance backdown through this period, was tower packing pluggage.

The primary packing, first stage demister, and second stage demister all experienced pluggage during normal operation due to the loss of flow through slurry recycle nozzles and the scaling of gypsum due to the process chemistry.

What follows is a short narrative describing the history of the various activities that affected or were affected by the subject troubleshooting program.

PRIMARY PACKING

Prior to late 1981, the major identified cause of pluggage in primary packing was the pluggage of the nozzles (which distributed slurry to the packing) with debris and scale picked up by the the recycle pumps. This pluggage problem was addressed by the installation of pump suction screens in late 1981. The screens, tested and recommended by the Scrubber O.E.M., greatly reduced nozzle pluggage which, in turn, doubled the scrubber system's capacity and availability to treat flue gas.

The problem that still remained to be addressed was the scaling due to the process chemistry.

MIST ELIMINATOR PACKING

The original control system for the washing of the tower mist eliminator packing was designed to permit large demands on the wash water supply system, sometimes in excess of 4,000 gpm. The original source for this wash water was the plant's service water system which could normally handle this demand. With NPDES, State restrictions, and a large positive water balance in the MLSES scrubber system, this service water (lake water) supply to the mist eliminator wash system had to be curtailed in 1980. The sources for this mist eliminator wash water have varied since this time from ash water to FGD system recycle water to low volume retention pond water. Continued mist eliminator pluggage occurred because of:

- inadequate washing of the packing as a result of low pressure and flow,
- the dissolved calcium sulfate in the wash waters, and
- the process chemistry in the upper loop.

WATER BALANCE

Experiences at MLSES, from the initial operation of Unit 1 in early 1977 through the present, have consistently proven that a net positive water balance exists. The consensus opinion of the plant personnel in 1979 was that this net positive water balance averaged 1,000 gpm. The NPDES compliance program provided segregation of plant wastewater into the following three (3) groups.

1. FGD -- Scrubber and sludge handling wastewater.
2. ASH -- Bottom ash, station sumps, and demineralizer wastewaters.
3. Low Volume -- Sanitary sewer effluent, lignite and plant area drainage.

After the completion of the NPDES compliance program in 1980, it was determined that the FGD system was the major contributor to the net positive water balance. In order to reduce the service water (lake water) input to this system and increase the system's ability to absorb plantsite rainfall, the following steps were taken.

1. Recycle FGD wastewater diluted with water from the low volume system was used for mist eliminator spray water to replace service water.
2. Recycle FGD wastewater was used for washdown water in the scrubbers and waste disposal areas to replace service water.
3. Use of water from the low volume system for all services in the limestone preparation area to replace service water.
4. Purchase and installation of a wastewater treatment plant to clean up FGD wastewater for use as mist eliminator spray water.

As a result of implementing these ideas, the net positive water balance has decreased to approximately 400 gpm as of November 1, 1982. With the completion of the wastewater treatment plant in mid-1984, TUGCo MLSES' FGD system was expected to approach zero discharge.

PROGRAM OBJECTIVES

The original objective of the EPRI sponsored program was to investigate the cause of the reported chemical scaling occurring inside the scrubber towers and to demonstrate a means of controlling or eliminating its formation. With the mechanical cause of packing pluggage eliminated by the suction screen installation discussed previously, the tower's availability became limited by the formation of calcium sulfate scale within the packing.

As the EPRI program progressed into the on-site test phase, three additional items were included in the scope of the program. These were:

1. Low Limestone Utilization
2. Positive FGD Water Balance
3. Testing of the New Packing Design

The objectives of the original test plan were expanded to aid TUGCo in examining these.

RESULTS OF TEST PROGRAM

The following sections present the results of the EPRI-sponsored phase of the FGD system reliability improvement program at Martin Lake. Information is presented on the initial characterization testing, as well as on the development of a plan to examine the ability to control the chemical scaling in the towers. The performance of four test towers over a three-month period is documented. In addition, observations on the overall utilization of limestone reagent for the FGD system are presented and recommendations of methods to improve it are discussed. Finally, the water balance around the FGD system is quantified and two approaches to reducing the excessive consumption of water by the scrubbers are presented.

CHARACTERIZATION TESTING

A brief visit was made by Radian engineers and chemists to Martin Lake in March, 1983, to collect samples from several operating modules to measure the concentrations of the various chemical species in the slurry, solid, and liquid phases of the process streams. In addition, plant operating personnel were consulted to gather specific information on the historical operating problems of the scrubbers. With this data, a comparison was made between the characteristics of the Martin Lake scrubbers and the limestone systems with which Radian has had extensive operating and design experience. From this comparison, alternatives to the operation and control of the scrubbers to satisfy the program objectives were identified.

The specific highlights of the characterization testing are:

- excess limestone concentrations in the absorber feed tank (upper loop slurry) ranged from 20 percent to 300 percent (four measurements);
- sulfite oxidation in the absorber feed tank (AFT) slurry ranged from 24 percent to 42 percent;
- the gypsum relative saturation in the AFT liquid phase ranged from 0.98 to 1.00;
- the gypsum relative saturation in the mist eliminator wash water was 1.10;

- the analysis of the scale forming in the tower packing and mist eliminators reported the material to be almost all calcium sulfate;
- the limestone product from the mill circuit averaged about 80 percent less than 325 mesh; and
- the limestone was of good purity (greater than 95 percent calcium) and relatively soft (Bond Work Index of about 6).

Additional information from TUGCo indicated that:

- chemical scaling in a tower's primary packing and mist eliminators resulted in significant reduction in gas treating capacity after only about 40 days;
- the volumes of mist eliminator wash water and pump seal water being used were contributing to a positive FGD system water balance;
- limestone was added to the scrubbers by manual control;
- the existing primary packing was not physically able to withstand cleaning of scale from its surface; and
- the FGD system on the three units were being retrofitted for forced oxidation.

Comparison of these results with past experiences identified two potential causes for the chemical scaling in the towers. These were:

- large excesses of limestone in the upper loop slurry, and
- high gypsum relative saturation in the mist eliminator wash water.

TEST PLAN

To determine the effect of reducing the excess of limestone in the AFT's and improving the mist eliminator wash, a plan was developed which outlined modification to four towers and long-term testing to document the impact on tower reliability. Four towers on Unit 3 were selected for the necessary modifications. The towers that were modified were 3A-200, 3A-300, 3B-200, and 3B-300. The modifications on the two "A" module tower were installation of a separate feed line for limestone slurry to the quenchers and use of an on/off type controller to regulate addition of limestone to the AFT and quenchers to maintain a pH setpoint. The same modifications were made on the "B" module towers. In addition, a small stream of slurry was taken from each "B" quencher recycle loop and fed to the "B" module AFT. The purpose of this was to increase the gypsum crystal concentration in the AFT to provide a greater number of crystallization sites for the calcium sulfate formed in the towers.

OPTIMIZATION TEST RESULTS

Chemical Scaling Observations

The modifications were completed by the end of the fall outage in 1983, and the test program evaluating the changes was begun in December, 1983, and lasted until the Unit 3 Spring outage in March, 1984. The performance of the test towers was monitored daily by recording such data as pressure drop, gas flow, pH, inlet SO_2, outlet SO_2, oxidation air flow, density, etc. In addition, slurry samples were collected routinely for analysis to determine the effect of the changes on the chemistry of the scrubbers. The success of the modifications was evaluated by inspecting the towers at times when they were taken off-line for maintenance or because of temporary unit outage. Photographs of the condition of the packing and mist eliminators for the test and non-test towers were taken during the inspections.

The results of the long-term testing showed that a dramatic reduction in the scaling rate in both the primary packing and the mist eliminators occurred as a result of the modifications made on the two "B" module towers. The results for the two "A" module towers were not as good, indicating that the recycle of the gypsum from the quenchers to the AFT was important in preventing scale growth. After 84 days of operation, no scale was found in the 3B-300 primary packing, and after 66 days of operation, 3B-200 had no scale in its packing.

Figures 4 and 5 are photographs of the bottom of the tower 3B-300 and tower 3B-200 primary packing, respectively, before the test program began. Tower 3B-300 had a new type of packing in it which Texas Utilities was interested in because of its sturdier construction. Tower 3B-200 had all new sections of the original style of packing. Figures 6 and 7 are photographs of the bottom of the primary packing for 3B-300 and 3B-200 at the end of the test period (84 days of operation for 3B-300 and 66 days for 3B-200). As indicated, no scale formation was found in either packing at the end of the test period in March. For comparison, tower 3C-200 showed approximately 60 percent pluggage of its primary packing after only 49 days of operation. Tower 3C-300, 3D-200, and 3D-300 showed similar scaling rates throughout the test program. Figure 8 is a photograph of the bottom of the packing in tower 3D-200 after 39 days of operation. The packing was at least 50 percent plugged with gypsum scale.

During the test tower inspections, the mist eliminators showed continued signs of scaling and pluggage. The solids were accumulating on the mist eliminators furthest from the point where wash headers entered the towers. The quality of the wash water was improved from that measured during the characterization visit by switching to a source very low in dissolved calcium sulfate. To improve the reliability of the mist eliminators, the wash system was upgraded by replacing the wash nozzles with higher flow designs. Tower 3B-300 was selected for a test of the improved wash. After 37 days of operation, the 3B-300 mist eliminator remained essentially scale-free. Figure 9 is a photograph of the lower mist eliminator at the end of the test. During this period, the limestone utilization in the 3B-300 upper loop recycle slurry

Figure 4. Bottom View of Tower 3B-300 Primary Packing Before Testing.

Figure 5. Bottom View of Tower 3B-200 Primary Packing Before Testing.

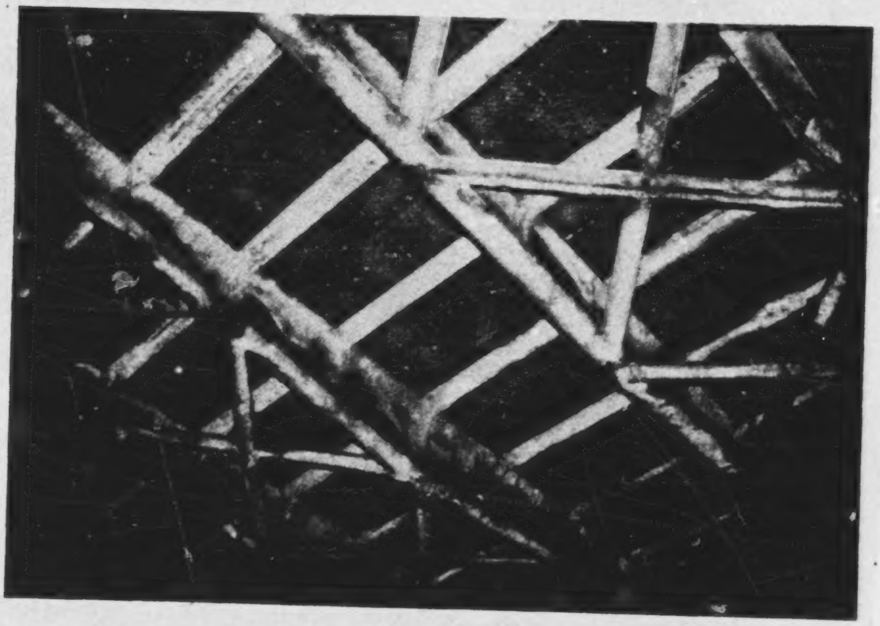


Figure 6. Bottom View of Tower 3B-300 Primary Packing After Testing (84 days).

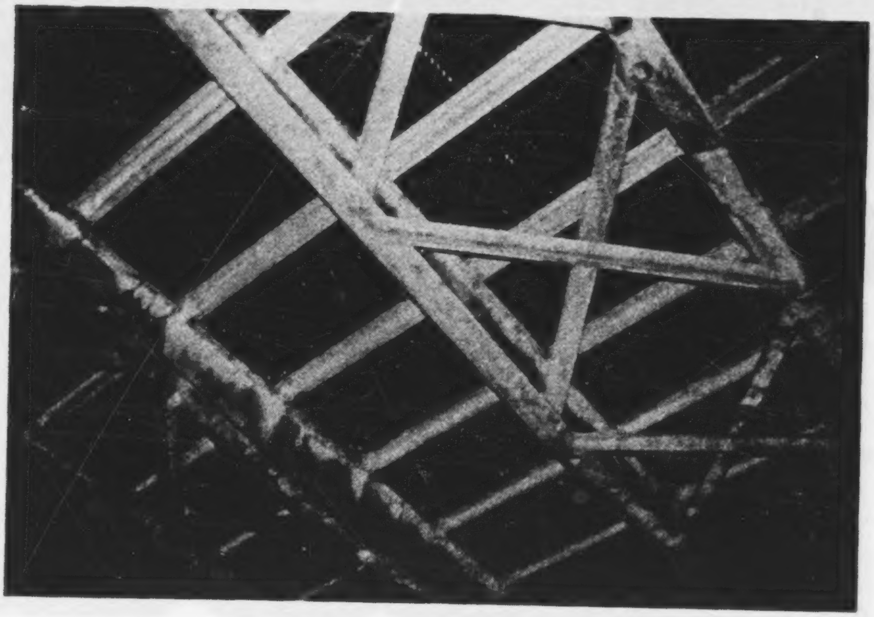


Figure 7. Bottom View of Tower 3B-200 Primary Packing After Testing (66 days).

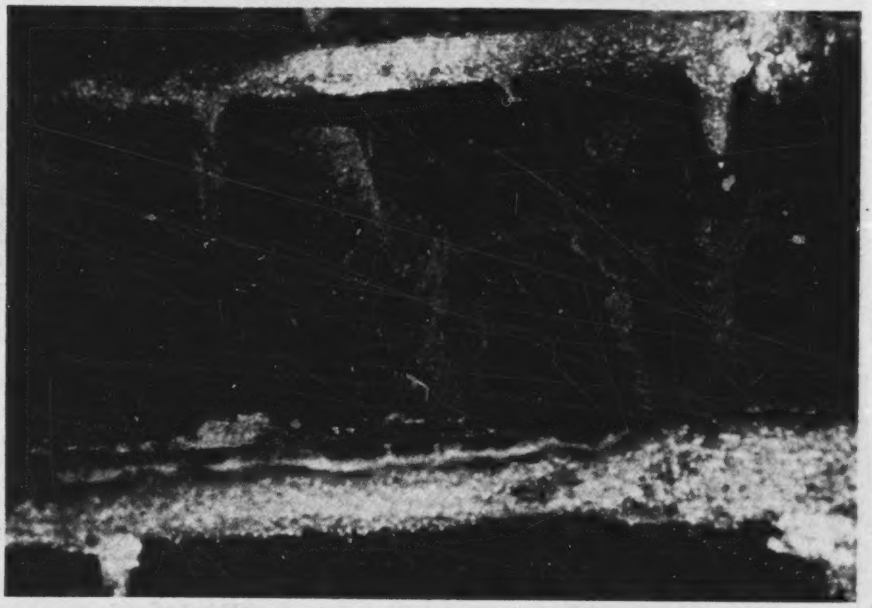


Figure 8. Bottom View of Tower 3D-200 Primary Packing After 39 Days of Operation.

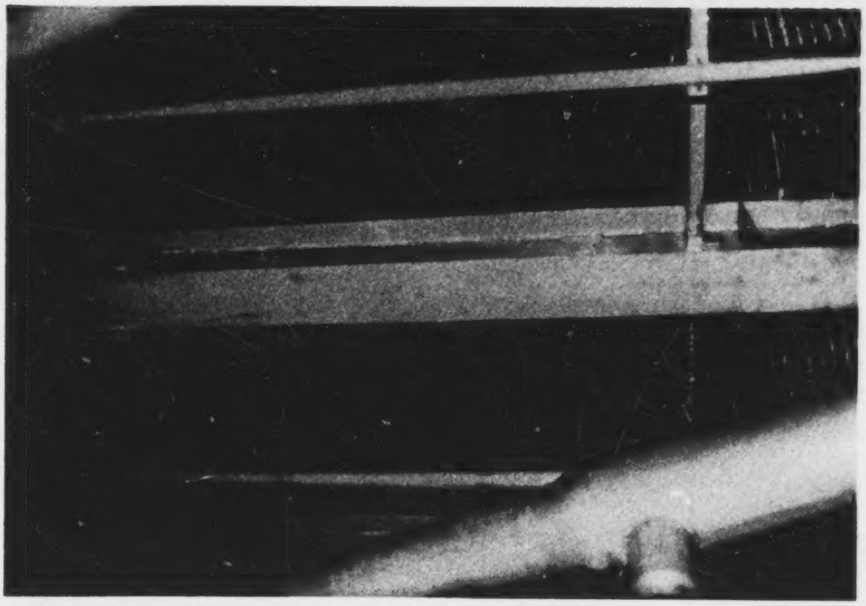


Figure 9. Bottom View of Tower 3B-300 Lower Mist Eliminator After 37 Day Test.

was controlled at 90 percent (average pH of 5.8) and the apparent solid sulfite oxidation due to gypsum recycle averaged 95 percent. In addition, the wash frequency was decreased to an average rate of 35 gpm for the total upper and lower face washes. This was a decrease of about 60 percent from the previous average wash rate of about 60 gpm per module.

During this same period, the experimental primary packing (Poly Manufacturing, Inc.) was under evaluation in the 3B-300 tower at MLSES. The SO_2 removal efficiencies of the new packing were measured to be equal or slightly above the O.E.M. packing for equivalent pressure drops. From a maintenance standpoint, the new packing was superior to the original O.E.M. packing. The new packing demonstrated improved durability and cleanability which, when coupled with greatly reduced scaling due to the chemical process improvements, should reduce the consumption rate of new units even further.

LIMESTONE UTILIZATION/SULFITE OXIDATION

TUGCo actively began to pursue marketing a commercial grade gypsum by-product when, in mid-1983, it became apparent that commercial grade gypsum could be produced consistently. A tighter control of process operation, coupled with an extensive analytical program, was initiated. The EPRI program supported this goal with its own sampling program, recommendation for instrumentation and control loop modifications, and study of the benefits of a finer limestone grind.

Samples of the scrubber recirculating slurry were collected routinely during the test period by Radian for analysis to investigate the effect that the modifications had on the chemistry of the test towers. Limestone utilization and sulfite oxidation were monitored closely. Initial analyses indicate that limestone utilization was lower than that seen during the characterization period. The average utilization for the analyses of the thickener underflow solids for Units 1, 2, and 3 was 78 percent for the period of December, 1983, through March, 1984. The decrease in utilization was probably due to the substantial increase in the coarseness of the limestone being produced by the ball mill circuits.

To analyze the potential improvement of limestone utilization that grinding modification could bring, corrective action was taken on one of four mill circuits to allow production of a finer limestone. The resulting limestone showed an increased reactivity in the scrubbers on Unit 3 similar to that seen during the characterization period. Figure 10 is a plot of the relationship observed between quencher pH and utilization. Recommendations by Radian to improve the mill circuit so that 85 to 90 percent would pass a 325 mesh screen were made.

The pH of the quencher/oxidation sump was shown to be an important factor in achieving maximum oxidation. The results of the testing defined a need to maintain a sump pH of 5.0 to 5.3 to optimize oxidation, quencher section SO_2 removal, and residual $CaCO_3$ levels. TUGCo implemented a control system for each tower quencher sump based on EPRI/Radian recommendations. This additional pH control loop supplements the absorber loop pH controls originally supplied.

In order for the pH control of the quencher sumps to be effective, higher reliability was necessary from the sump pH monitoring instruments. The existing pH system, which has been in service since 1979 on all towers, was prone to problems with electrical connectors, bulb electrode malfunction, and signal noise between local preamp and remote processor. EPRI recommended, and TUGCo purchased, a state-of-the-art pH system. This system locates its complete electronics package at the sampling point and transmits a 4 to 20 m.a. signal to the control room. To-date, this equipment has performed well.

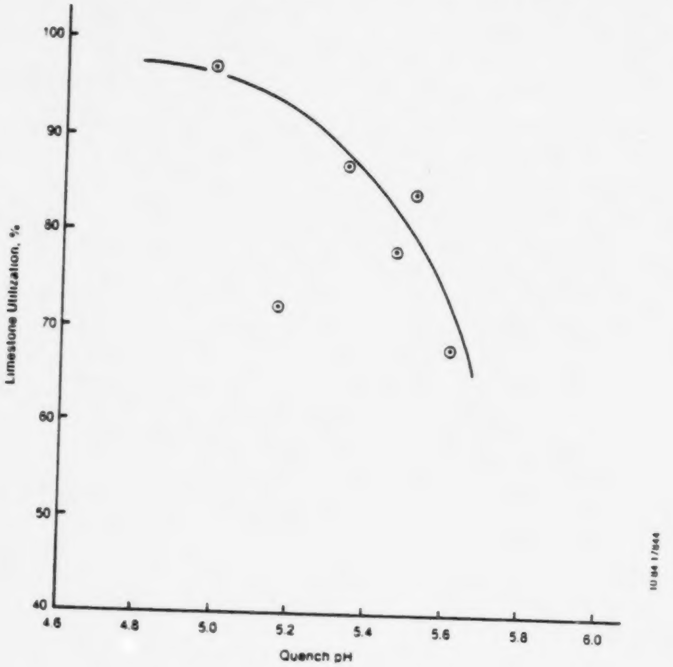


Figure 10. Quench pH Versus Limestone Utilization - Demonstration Testing - Fine Limestone (80% < 325 mesh).

Sulfite oxidation was monitored on the test towers since Texas Utilities expects to sell the gypsum produced in the scrubbers for wallboard manufacture. It was important to document the effect that the modifications had on the oxidation efficiency in the towers. The data collected indicate that there was no adverse effect on the oxidation of sulfite in the quenchers due to splitting the feed of limestone or due to recycling slurry from the quenchers to the AFT. In fact, due to lower pH operation of the AFT, the natural oxidation of sulfite in the upper loop increased from an average of about 35 percent to greater than 90 percent. This should substantially decrease the load on the forced oxidation system which operates in the quenchers. It may be possible to operate with a lower than originally designed air rate and still achieve complete oxidation there.

WATER BALANCE

The FGD water balance at Martin Lake has historically been positive, requiring the use of expensive wastewater treatment equipment (described earlier) to process the system water to a quality suitable for reuse in the FGD system to replace lake water. As part of the EPRI program, information was collected on the FGD system balance to identify ways to reduce the water requirements of the scrubbers, with the goal being zero net water balance for the system with minimum use of the wastewater treatment plant.

The expected benefit of this mode of operation would be better control of the density in the AFT's and quenchers, a reduction in operating and maintenance costs associated with the wastewater treatment plant, and reduction in pond maintenance dealing with the system discharges. The result of the FGD water balance investigations presented in Table 3 indicate that the system operated with an average positive balance of 1,300 gpm excluding rainfall contributions during the period of December, 1983, to March, 1984. The largest, single user of water within the FGD system was pump and agitator seals. The next largest user was the mist eliminator wash. By switching to mechanical seals on the pumps, reducing the frequency of mist eliminator wash according to the recommendations presented in the report, and switching the source of limestone ball mill water, the FGD system could be taken to over 1,000 gpm negative, not including rainfall. Of course the installation of mechanical seals on such a wide scale is a very difficult task and involves a high capital outlay. The recommended approach was to test several of the seals on the market at this time and phase in their use as practical.

TABLE 3. MARTIN LAKE FGD SYSTEM WATER BALANCE DURING TEST PERIOD 12/83 - 3/84

	Quantity, gpm
Water In	
Pump/Agitator Seal Water	1600
Mist Eliminator Wash	1200
Limestone Grinding	300
Rainfall Runoff	600
Water Out	
Vaporized	1700
Associated with Sludge	100
Net Balance	+1900

The negative side of minimum treatment plant operation and zero discharge is the eventual buildup of dissolved chlorides in the liquor. The projected steady-state level is about 7,000 ppm. At this concentration, there must be some type of chloride purge if the 200 ppm limit on the dried gypsum sent to wallboard manufacture is to be met. Currently, TUGCo can use their wastewater treatment equipment to remove the chlorides. An alternative would be to install filter cake washing equipment to remove the chlorides.

FULL SCALE MODIFICATIONS

Based on the previously discussed EPRI test program results and estimated yearly savings of $3,500,000 in packing replacement and labor, the decision was made by Texas Utilities to install the split limestone/gypsum recycle system and pH upgrade on all three (3) units during the Fall, 1984, outages. A Capital Expenditure Authorization was approved on May 1, 1984, for $194,000 per unit or $582,000 total cost for the installation on all three (3) units. With projected yearly savings of $3,500,000, this resulted in a payout time of less than 3 months.

The new system includes new pH transmitters, piping and meters; use of the existing scrubber system programmable controllers for pH control; piping and control valves for the split limestone/gypsum recycle system. Because of Radian's involvement in the entire program (under contract to EPRI), the decision was made to contract their services for detailed engineering work on the project. TUGCo also opted for the more durable primary packing tested during this program to be installed in all towers.

Consideration is still being given to the water balance improvements and limestone fineness improvements proposed by the EPRI program. The water balance improvements would be costly to implement ($1,100,000 for mechanical seals for all scrubber recycle pumps). TUGCo, through the use of wastewater treatment plant product water, has converted the pump seal water from a service water (lake water) consumer to another point of FGD system water recycle. This took away the immediate problem of pump seal water usage impacting the FGD system water balance.

TUGCo is seriously considering EPRI recommendations regarding limestone fineness as they relate to limestone utilization in the scrubbers and unreacted limestone in the scrubber waste product. TUGCo's intention to market by-product gypsum will require tight control on this unreacted limestone.

EQUIPMENT DESIGN

The following is a discussion of the modification to existing equipment and installation of new equipment that was required to implement the process changes that were recommended by EPRI and subsequently approved for implementation by the utility's FGD task force.

Process Piping

A. Reagent (Limestone) Feed Lines to the Quencher:
A stainless steel reagent feed line was tapped downstream of the existing flowmeter and upstream of the existing control valve. The pipe has a reagent control valve regulating the addition of limestone to the quencher sump. Adequate isolation valves and flushing provisions were also installed.

B. Gypsum Recycle Lines From Quencher Pump Discharge to AFT:
The individual tower quencher pump discharge line was tapped downstream of both pump discharge valves (one tap per tower). This new pipe was routed to the top of the AFT and connected to an existing opening.

C. pH Sample Line Revisions:
In addition to the above two (2) new lines, all of the existing pH sample lines were redesigned and relocated for more reliable sample delivery.

Instrumentation

A. The existing scrubber system programmable controllers were utilized to accurately control the process. Additional input/output cards were the only upgrade needed.

B. The existing pH meters and recorders were replaced with state-of-the-art equipment.

C. All density and pH readouts were changed to digital indicators and mounted on the control panels.

Accessibility

A. The existing AFT reagent feed valve accessibility was improved on all 12 AFT's.

B. All of the new quencher reagent feed valves (control, isolation, flush, and drain) were installed for ease of access by Operations and Maintenance personnel.

C. All of the pH sample cells were relocated to be accessible to Chemical personnel.

Analytical Equipment

To adequately support the revised and tightened control of the scrubber process, the Chemical Support Group will need to routinely analyze directly for calcium carbonate and calcium sulfite. To effectively provide the necessary analytical results in a timely, cost-effective manner, a sample titrator-analyzer system with hook up to a PC for data reduction and logging was purchased. With this system, one chemist can collect, analyze, and report oxidation and limestone utilization for each operating AFT, quencher, and thickener within an eight hour period.

Control Philosophy

The objective of the control philosophy was simplicity. The only necessary interlock is obtained within the scrubber system PC. This is a tower in-service interlock which is incorporated into the reagent feed control valve operating circuit.

Manual back-up provisions are incorporated (off-on-auto control switches). Also, written instructions are being issued for Operations personnel to define operating options and provide a complete troubleshooting guide for operation with the new process control scheme.

CONCLUSION

As a result of the EPRI sponsored program at Martin Lake, proposed solutions to FGD system problems were tested and demonstrated to be effective. These solutions were put forth by both TUGCo with its Scrubber Task Force and EPRI with Radian.

TUGCo has implemented these solutions to prevent scaling of the absorber packing and estimates that these changes will result in savings of $2.5 to $3.5 million/year in future years' operating and maintenance costs when compared to 1984 costs. These solutions have also improved limestone utilization, and TUGCo estimates that reagent costs will be reduced by about $0.5 million/year when compared to 1984 costs. The other recommendations for prevention of mist eliminator scaling and for improving water balance are under investigation by Martin Lake personnel. Cost savings associated with these improvements have not as yet been estimated.

The value that the program provided TUGCo in the area of information exchange with the EPRI and Radian personnel involved cannot be measured. It must suffice to say that TUGCo personnel learned much about their FGD system that they would not have had the opportunity to learn without the program.

AVAILABILITY ANALYSES FOR FLUE GAS DESULFURIZATION IMPROVEMENT DECISIONS

Albert R. Cunningham
Philadelphia Electric Company

Morton J. Smith
Pickard, Lowe and Garrick, Inc.

ABSTRACT

A recent study was sponsored by the Electric Power Research Institute (EPRI) to determine the usefulness of availability analysis techniques for guiding decisions involving improvements on flue gas desulfurization (FGD) systems. This study was directed by Mr. Morton J. Smith, and involved the active participation of personnel at Philadelphia Electric Company (PECo) under the direction of Mr. Albert R. Cunningham.

The study concluded that availability analyses can provide significant insight into the consequences of alternative decisions faced by the responsible FGD plant personnel. These decisions can relate to matters of FGD design, operation, and/or maintenance, and can affect various levels of the system hierarchy from the overall FGD system to individual components. In addition, the results indicated that these analyses can provide plant personnel with additional value at the process variable level if the availability analysis can be combined with FGD performance models.

INTRODUCTION

In July, 1984, EPRI awarded a contract to study the usefulness of availability analysis techniques for FGD applications. Specifically, EPRI was interested in the extent to which modeling techniques, such as UNIRAM, could aid plant personnel in selecting options for improving FGD availability.

Philadelphia Electric Company volunteered to support this study by permitting the FGD system at their Cromby Unit 1 to be used as the demonstration system. In addition, PECo provided personnel to assist with the analysis, run the selected computer analysis code, and to assist in presentations to PECo management. PECo also provided access to the key plant personnel responsible for the day-to-day operations and maintenance of the FGD system.

2. SYSTEM OVERVIEW

Cromby Station is located in the town of Phoenixville, Pa., which is northwest of Philadelphia. It consists of one coal-fired boiler and one oil-fired boiler capable of generating approximately 147 and 211 mw's net respectively. The units are essentially base loaded, although they are subject to cycling because of the use of economic dispatch for system loading. FGD characteristics of Cromby Unit 1 are shown in Table 1.

TABLE 1. CROMBY UNIT 1 AND FGD CHARACTERISTICS

Location	Phoenixville, PA
Size	147 mw net
Fuel	Coal
Commercial Operation	1954
Boiler Manufacturer	Babcock and Wilcox
Turbine Generator Manufacturer	General Electric
FGD System Commercial Operation	January, 1982
FGD Architect/Engineer	United Engineers & Constructors
FGD System Initial Cost	$55 Million
FGD Scrubbing Agent	Magnesium Oxide (MgO)

The regenerable magnesium oxide (MgO) flue gas desulfurization system (FGD) selected by the Philadelphia Electric Co. for the Cromby installation utilizes a negative pressure, induced draft scrubber system. The system consists of three parallel scrubber trains, each of which is designed to scrub one half of the flue gas from the Unit No. 1 Boiler. Two trains are in continuous operation while the third is a complete spare. Flue gas from the boiler I.D. fans is distributed to each of the two operating trains through a supply plenum. Gas is drawn through the particulate scrubbing system, which consists of a slurry of ash particles in river water whose pH is controlled by the addition of a caustic solution. Each scrubbing unit is designed to remove at least 95% of the incoming SO2 and operate over a three to one turn-down range to accommodate periods of reduced boiler gas flow. Flue gas undergoes a two-stage dry particulate removal before entering the first section of the FGD system. The scrubber also humidifies and cools the flue gas. Before entering the stack, the wet demisted SO2 scrubber exit gas is joined by a heated gas flow from an oil-fired reheater. The reheater prevents condensation on the scrubber booster fan impellor and reduces absorption of sulfuric acid mist from the scrubber flue gas. It reduces the formation of a visible stack plume and increases the buoyant atmospheric dispertion of the stack gas. To comply with DER standards, SO2 emissions at Cromby Station may not exceed the following limits: 0.9 lbs./million btu (30-day average), 1.2 lbs./million btu (daily average 2 days out of 30), 1.44 lbs./million btu (daily maximum).

The use of this MgO material is relatively unique in the industry since most systems are of the non-regenerable lime-limestone variety. The only other similar systems are located at PECo's Eddystone Station. The Cromby system began operation in 1981. It had a capital cost of about $55 million, and has had an annual maintenance budget of approximately $2.0 million. The system uses about $1.8 million of regenerative and virgin MgO annually.

Cromby's FGD system consists of the six major "subsystems" shown in Figure 1 (below). The MgO supply is provided by the regeneration facility, with supplementary material from suppliers of virgin MgO to make up losses. Although this supply function is critical to the economic viability of the FGD system, the current analysis was focused on the in-plant subsystems. These subsystems include MgO handling, boiler gas input, scrubbing, particulate processing and disposal, and solids separation. For purposes of the current analysis, the particulate processing and disposal subsystem was omitted so that emphasis could be put on those subsystems considered most critical in terms of FGD availability.

There are a considerable number of redundant paths and operational workarounds in this system. For example, there are two MgO slaking systems, three scrubber trains (two of three provide full capability, and one of three provides 50% capability), two centrifuge-dryer functions. Further, there are preventive maintenance programs implemented to reduce both frequency and duration of forced outages.

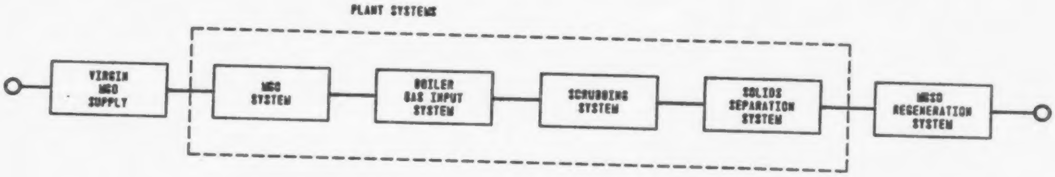


FIGURE 1. PLANT SYSTEMS

3. METHODOLOGY

As stated above, the primary study objective was to determine the extent to which availability analyses can be used by plant personnel in making decisions affecting FGD availability. To achieve this objective, a 9-step analysis process was followed as shown in Table 2:

TABLE 2. ANALYSIS PROCESS

- Success Criteria/Intended Uses
    - Availability Measures
        - Functional Diagrams
            - Availability Diagams
                - Input Data Base
                    - Computer Modeling/Analysis (Baseline)
                        - Results Assessment
                            - System Mods Definition
                                - Decision Impact Evaluation

The initial step in this process was to define the criteria for judging FGD availability (i.e., its ability to support the unit's output) and to make an initial determination of the potential uses of these analyses for FGD decision making; e.g., selection of preventive maintenance programs, definition of hardware improvements.

This step was followed by construction of functional flow diagrams for the major FGD equipment groupings. These diagrams highlighted the major equipment items and their functional interactions; e.g., SO2 surge tank, SO2 scrubber secondary demister. Each of these diagrams (see sample in Figure 2) was accompanied by a brief description of the potential modes of failure for each piece of equipment, and the anticipated consequences of these failures on the availability of the FGD system.

The measures used for quantifying FGD availability were selected as equivalent availability (EA), equivalent unavailability (EU) and the equivalent number of days that the FGD system could be expected to support Unit 1 operations. Equivalent availability is defined as the equivalent percent of the period hours that the FGD system could be expected to operate at full capability. As an equation, EA is:

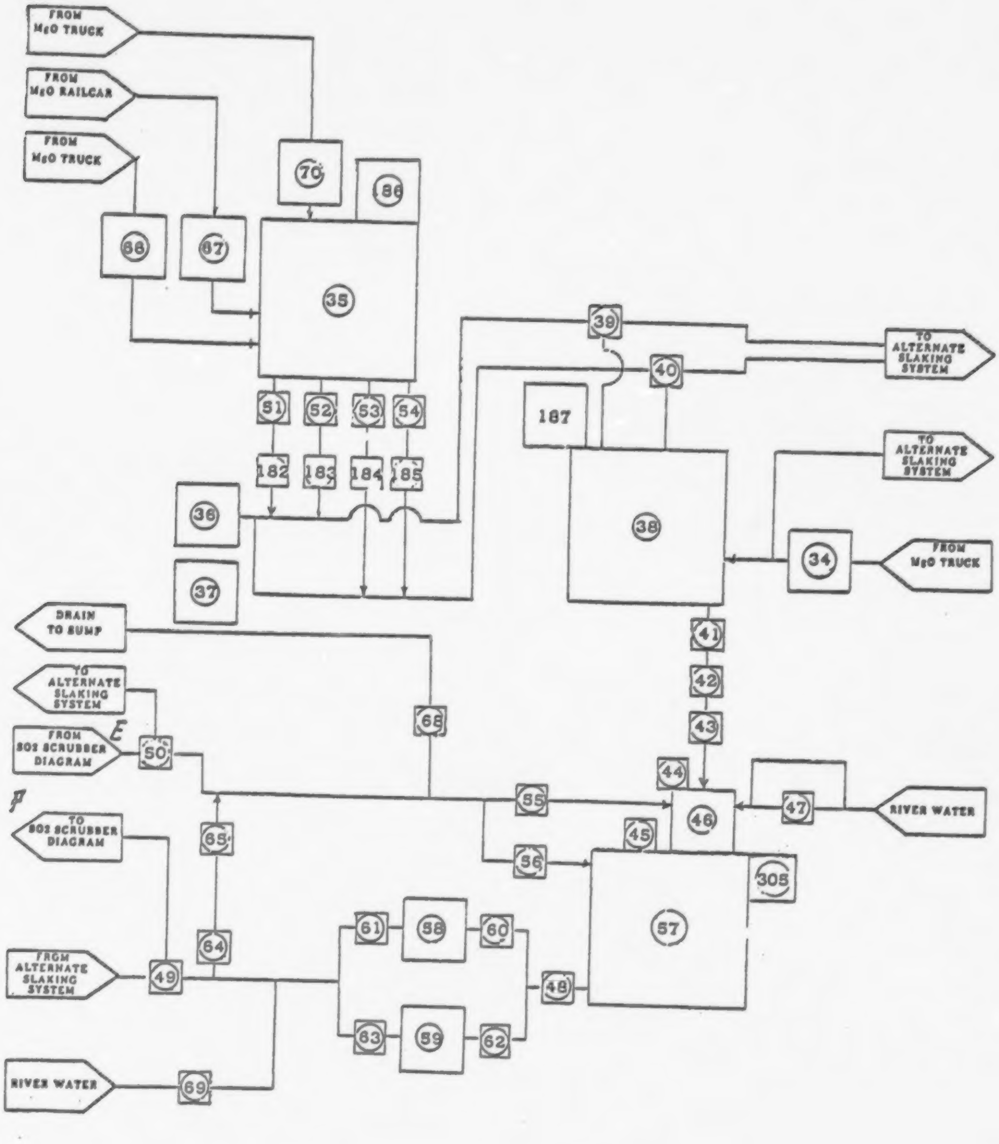

FROM MgO TRUCK
FROM MgO RAILCAR
FROM MgO TRUCK
70
186
66
67
35
39
40
TO ALTERNATE SLAKING SYSTEM
187
51
52
53
54
182
183
184
185
36
37
38
TO ALTERNATE SLAKING SYSTEM
34
FROM MgO TRUCK
DRAIN TO SUMP
41
42
43
TO ALTERNATE SLAKING SYSTEM
68
E
FROM SO2 SCRUBBER DIAGRAM
50
44
46
47
RIVER WATER
55
P
TO SO2 SCRUBBER DIAGRAM
65
45
56
305
57
61
58
60
64
FROM ALTERNATE SLAKING SYSTEM
49
48
63
59
62
RIVER WATER
69

FIGURE 2. FUNCTIONAL DIAGRAM MgO SLAKING SYSTEM (SUPPORT SYSTEM)

$$EA = \frac{\text{Available Hours - Equivalent Derated Hours}}{\text{Period Hours}}, \text{ and}$$

$$EU = 100\% - EA$$

(NOTE: For this analysis, FGD operation was required an average of only 337 days per year. The system was not required during the Unit 1 annual outage which averaged 28 days.)

Given the above information, availability block diagrams were constructed (see sample in Figure 3) to represent the combination of equipment necessary for the FGD system to support various levels of unit operation. These diagrams and the input data for each piece of equipment (mean time between equipment failures {MTBF} and mean time to restore {MTTR} the equipment to operational status) represented the baseline model for the system.

This model was analyzed using the UNIRAM computer analysis code. This analysis code, which was developed by EPRI to perform unit-level availability analyses, was run by PECo on their IBM computer. The analysis results were discussed with the responsible results engineer and his staff, and appropriate changes were made to make the model more accurately represent the operational FGD system.

Finally, operational alternatives confronting the plant personnel were translated into model changes, and the computer was used to produce the resulting numerical changes in the measures of FGD availability. These results were tabulated and plotted for presentation to PECo management to demonstrate the potential value of these analysis techniques (see Section 4.3).

4. ANALYSIS

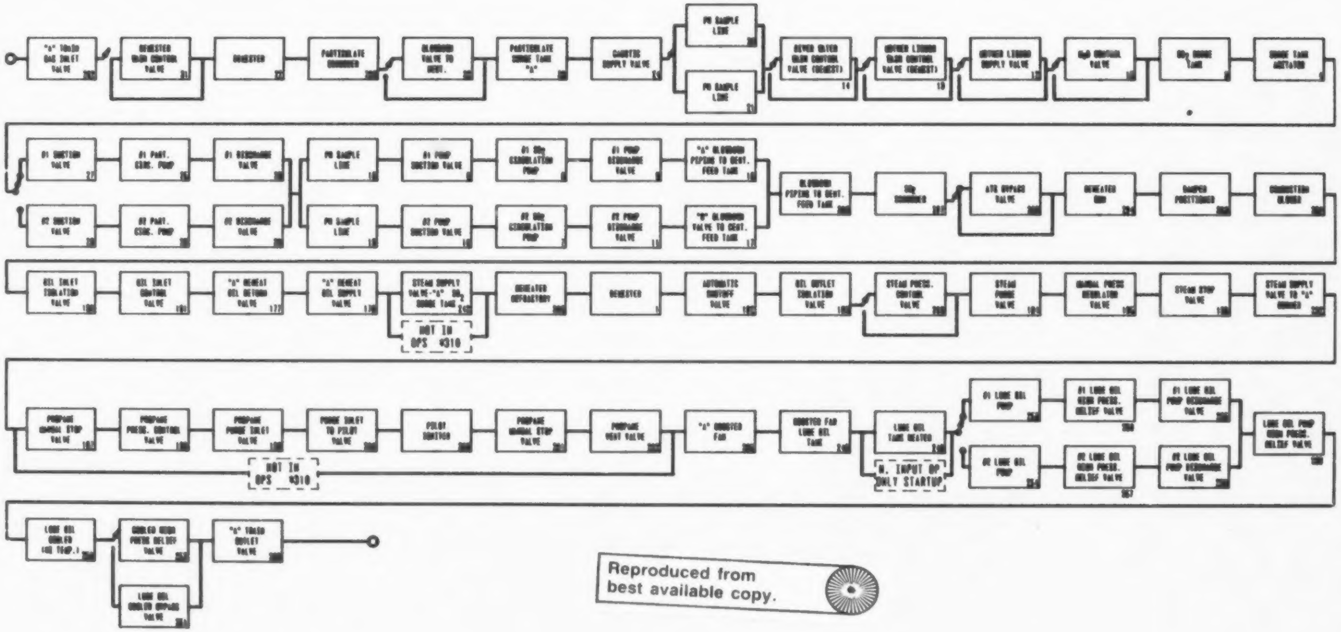
4.1 Key Assumptions

In order to properly interpret the analysis results, it is important to understand some of the assumptions underlying the analysis. First, the purpose of the analysis was to develop a tool for plant personnel to obtain timely insight into the need for system changes and their relative impact on FGD availability. Therefore, potential improvement actions were assessed on the basis of their relative contribution to availability improvement, rather than on the absolute values of the estimated measures.

PHILADELPHIA ELECTRIC CO.
AVAILABILITY/RELIABILITY GROUP
AVAILABILITY BLOCK DIAGRAMS FOR
CROMBY STATION FGD SCRUBBER
SEPTEMBER 1984

SCRUBBER TRAIN "A"

PHILADELPHIA ELECTRIC CO.
AVAILABILITY/RELIABILITY GROUP
AVAILABILITY BLOCK DIAGRAMS FOR
CROMBY STATION FGD SCRUBBER
SEPTEMBER 1984


PARTICULATE SCRUBBER
PARTICULATE SURGE TANK "A"
CAUSTIC SUPPLY VALVE
PH SAMPLE LINE
PH SAMPLE LINE
SO2 SURGE TANK
#1 PART. CIRC. PUMP
#2 PART. CIRC. PUMP
#1 SO2 CIRCULATION PUMP
#2 SO2 CIRCULATION PUMP
"A" BLOWDOWN PIPING TO CENT. FEED TANK
"B" BLOWDOWN VALVE TO CENT. FEED TANK
ATS BYPASS VALVE
REHEATER
STEAM SUPPLY VALVE-"A" SO2 SURGE TANK
NOT IN OPS *310
AUTOMATIC SHUTOFF VALVE
STEAM PRESS. CONTROL VALVE
PROPANE PRESS. CONTROL VALVE
PILOT IGNITOR
PROPANE VENT VALVE
"A" BOOSTER FAN
LUBE OIL TANK HEATER
N. INPUT OF ONLY STARTUP
#1 LUBE OIL PUMP
#2 LUBE OIL PUMP
LUBE OIL PUMP HIGH PRESS. RELIEF VALVE
NOT IN OPS *310
LUBE OIL COOLER
"A" TRAIN OUTLET VALVE

Reproduced from
best available copy.

* OPS = OPERATIONAL STARTUP

FIGURE 3. AVAILABILITY BLOCK DIAGRAM

Second, the analysis models included all of those equipment items that were considered of most concern to the plant staff. These include most of the mechanical and electromechanical items, and only indirectly include the electrical instrumentation and control equipment. There were approximately 500 equipment items in the initial model.

Third, the analysis results are believed to have understated the availability of the FGD system as it performed in the field. The analysis computer code, for example, assumed that 11 redundant paths were active redundant when, in fact, most paths were standby redundant with highly reliable switching. Also, the benefits of time delays were not included in the availability estimates; that is, there are conditions under which an inoperable equipment item or subsystem can be repaired before it affects overall system availability. For example, the existence of storage points (e.g., MgO storage tank, $MgSO_3$ surge tank) throughout the system can compensate for some failures upstream or downstream of the failures. Also, there are times when the accumulated emissions are sufficiently below the allowed standards to permit the unit to continue operation for a period during which the FGD system may be inoperable.

4.2 Decision Alternatives

The availability analyses were used to evaluate the potential impact of the following types of decisions on FGD availability:

- Equipment Changes
- Use of Operational Workarounds
- Selection of Preventive Maintenance Schedules
- Hardware Configuration Changes
- Spare Parts Provisioning

In order to evaluate the potential impact of these types of decisions, the analyses addressed the following types of questions, which were asked by the results engineer and his staff:

1. What level of FGD availability would have been expected prior to the design changes and operational workarounds implemented since start of commercial operation?

2. Which equipment would have been identified as the primary contributors to FGD unavailability prior to implementation of the above design and operational changes?

3. Where in the current FGD configuration are the primary sources of unavailability problems?

4. What is the expected impact of extending the interval between scrubber train preventive maintenance from 9 weeks to 18 weeks?

5. Where in the system would cross-switching be most beneficial--between the centrifuges? Elsewhere in the centrifuge--dryer trains?

6. What is the potential impact of modifying the configuration of the MgSO3 silo?

7. Are there points in the system where hardware modifications could significantly reduce the load on the operations/maintenance team?

8. Would an operational procedure for failure mitigation be of significant value to FGD availability?

It should be noted from these questions and the analysis methodology that the analysis follows an iterative process. Questions are developed by analysis of a specified model, and these questions are translated into model changes. Analysis of each succeeding model provides insight for further investigation of improvement options.

4.3 Results

The analyses involved evaluation of about 10 models. The results for the baseline system (i.e., as-designed system) are shown in Table 3 (Expected Availability Levels) and Table 4 (Major Contributors to FGD Unavailability).

TABLE 3. EXPECTED AVAILABILITY LEVELS FOR AS-DESIGNED SYSTEMS

Availability Measures		Values	
Equivalent Availability		86.8%	
Equivalent Unavailability		13.2%	
Expected Number Days/Year*	- 100% Capability	276	
	- 50% Capability	34	337 Days
	- 0% Capability		

*Assumes Average Cromby 1 Scheduled Outage Duration of 4 Weeks/Year (365 - 28 = 337 Days of Possible Operation/Year)

TABLE 4. MAJOR CONTRIBUTORS TO UNAVAILABILITY OF AS-DESIGNED SYSTEM

Configuration and Equipment	Maximum Improvement* In-As-Designed (Percent)	Criticality Ranking
Scrubber Trains "Group"	5.9	1
SO_2 Scrubber	3.4	3
SO_2 Demister	1.6	5
Rh Refractory	1.3	6
Particulate Scrubber	1.1	7
SO_2 Surge Tank	0.7	10
Blowdown Piping to Centrifuge Tank	0.5	12
Other (18 items/train x 3 trains = 54 items)	-	-
Solids Separation "Group"	4.4	2
$MgSO_3$ Silo	2.8	4
Centrifuge Feed Recirculation Line	0.6	11
Centrifuge Feed Tank	0.5	13
Other (13 items)	-	-
B Centrifuge - Dryer Train	1.0	8
Centrifuge	0.7	19
Other (28 items)	-	-
A Centrifuge - Dryer Train	1.0	8
Centrifuge	0.7	19
Other (28 items)	-	-

*Assumes Specified Configuration or Equipment has Availability = 100%.

Table 3 shows the computed EA and EU values for the system, as well as the expected number of days at full capability, 50% capability and zero capability. Note that these days total 337 rather than 365 because the system is not required to support Cromby 1 operations during the annual outages, which average 28 days. The "critical items list" in Table 4 shows the major contributors to system unavailability, the amount of improvement in system availability to be gained by making a specific piece of equipment or group of equipments perfectly available (i.e., availability = 100%), and the ranking of each piece of equipment and equipment group in terms of its potential impact on FGD availability.

Similar output was generated for the other system configurations which were evaluated successively after determining from each analysis model the most potentially beneficial approaches to FGD availability improvement. Table 5 summarizes some of these analysis cases in improvements and their impact on the FGD availability measures. Some of the implications of these and other analysis results for PECo include the following:

- In retrospect, the actions taken by the plant staff to mitigate the impact of scrubber train problems resulted in a significant impact on FGD availability; e.g., 36% reduction in FGD unavailability.
- The MgSO3 silo modification would provide the greatest future improvement in FGD availability; e.g., reduce the unavailability by about 18%.
- The impact of the two potential changes for the centrifuges would have a significant, but comparable, effect on FGD availability; e.g., reduce the unavailability by about 9.5%.

5. CONCLUSIONS

This demonstration project, which was funded by EPRI and strongly supported by PECo, indicates that availability analyses can be used effectively for improving FGD system availability. These analyses can be performed in near real-time to support FGD improvement decisions by plant personnel. In fact, the analyses process provides side benefits for the plant (e.g., the use of functional block diagrams for training), as well as guidance for establishing a focus for collecting and assessing operations and maintenance data for FGD systems.

Further, these analyses can be updated as new information is obtained from system operation, and thereby provide plant personnel with improvement program guidance throughout the system's lifetime. For this reason, the analyses can be useful for evaluating planned systems, as well as operational ones. As with any other engineering analyses, the degree of confidence in the results will increase as the project moves from the conceptual design phase through operations and maintenance.

TABLE 5. SUMMARY OF AVAILABILITY MEASURES (AS-DESIGNED THROUGH SOME RECENT SUGGESTED CHANGES)

Analysis Results (Preliminary)	October 1984 System				
	As-Designed System	With Scrubber PM and Piping Change	With $MgSO_3$ Silo Change	With Centrifuge Cross-Over	With Spare Centrifuge Bowl
Equivalent Availability	86.8%	91.5%	93.0%	92.2%	92.4%
Equivalent Unavailability	13.2%	8.5%	7.0%	7.8%	7.6%
Expected Number Days/Year*					
(100% Capability)	276	307	311	308	309
(50% Capability)	34	6	6	6	6
(0% Capability)	27	24	20	23	22

*Assumes an average Cromby 1 scheduled outage of 4 weeks (337 days/year required for operation of the FGD system).

All of these benefits appear achievable, but not without the commitment of time and resources. Personnel must be trained to perform the analysis steps and use the appropriate tools. These personnel must learn to interpret the results of the analysis properly in the context of the operational use of the system. Plant personnel must learn the benefits and limitations of these analyses so that the results are interpreted properly and will lead to appropriate questions by plant personnel.

Finally, this study again showed that there is no substitute for the experience and knowledge of the availability analyst, designers, and plant personnel. The analysis techniques are merely tools, and as such, they must be used by knowledgeable, trained people in order to derive the potential benefits of these analyses.

Session 4, Part II: CHEMISTRY/REAGENT PREPARATION

Dorothy A. Stewart, Chairwoman
Electric Power Research Institute
Palo Alto, CA

A STUDY OF SULFUR-NITROGEN COMPOUNDS IN WET LIME/LIMESTONE FGD SYSTEMS

by: James B. Jarvis and Peter A. Nassos
Radian Corporation
Austin, Texas 78766

Dorothy A. Stewart
Electric Power Research Institute
Palo Alto, California 94303

ABSTRACT

This paper summarizes the results of an EPRI-sponsored program to study the relationships between sulfur-nitrogen (S-N) compounds and the wet lime/limestone FGD process. S-N compounds have been identified in the Arapahoe pilot-scale FGD system and are formed through a liquid phase reaction between SO_2 and NO_x absorbed from boiler flue gas.

The program objectives were to identify the factors which promote S-N compound formation in wet FGD systems and determine if the presence of these compounds changes system performance. A three-phase program was conducted which included analytical methods development, bench-scale process simulation, and pilot testing at EPRI's Arapahoe test facility.

The test results include the identification of various S-N species in solution and a description of how FGD process conditions effect NO_x removal, S-N formation, and the steady-state concentrations of S-N related species in FGD systems. The test results indicate that the accumulation of S-N compounds can cause a decrease in both SO_2 removal efficiency and operating pH. In most systems, however, the concentrations of S-N compounds are expected to be low enough such that the impact on SO_2 removal efficiency is not significant.

Prepared for Presentation at EPA/EPRI Symposium on Flue Gas Desulfurization Cincinnati, Ohio, June 4-7, 1985.

INTRODUCTION

Sulfur-nitrogen (S-N) compounds have been identified in scrubbing slurry from the Arapahoe pilot-scale flue gas desulfurization (FGD) system. These compounds, which contain a covalent sulfur-nitrogen bond, are formed through a reaction between the NO_x and SO_2 absorbed from boiler flue gas.

Radian was contracted by the Electric Power Research Institute to conduct a study of the relationships between S-N compounds and the wet lime/limestone FGD process. The primary program objectives were to:

1) Determine quantitatively which S-N compounds form in FGD systems;

2) Determine how process conditions affect the formation and accumulation of sulfur-nitrogen compounds; and

3) Determine if the presence of sulfur-nitrogen compounds results in changes in process operation; i.e., SO_2 removal, NO_x removal, limestone reagent ratio, waste solids characteristics, and process chemistry.

A three-phase program was conducted to address these issues. The first phase consisted of analytical methods development. The objective of this work was to produce analytical techniques which would be capable of measuring the concentrations of S-N compounds against a background of ions typically present in FGD slurry. A number of new or modified techniques were developed for this purpose. The second phase consisted of a series of laboratory tests. These tests were conducted using Radian's bench-scale FGD system and were aimed at identifying the variables influencing the formation rate of S-N compounds. These results were used to develop a test plan for pilot-scale testing. The pilot tests, which constituted the third phase of the test program, were conducted at EPRI's Arapahoe test facility in Denver, Colorado. On-site testing at Arapahoe was conducted between January and May of 1984.

BACKGROUND

Sulfur-nitrogen compounds were identified in FGD scrubbing liquor during a previous EPRI test program conducted at the Arapahoe facility. This discovery came about largely through an inability to close ionic balances on liquid samples taken during the operation of the pilot scrubber system. An excess of cations was measured which implied that anionic species were present in a form not previously accounted for. Further investigation indicated that the bulk of the unaccounted for anions were S-N compounds.

Research on the formation and decomposition of S-N compounds has been conducted in conjunction with the development of aqueous NO_x removal systems and the study of acid rain. However, these efforts did not specifically address the formation of S-N species in lime/limestone systems. Based on this information, a reaction scheme was prepared illustrating the possible pathways for the formation and decomposition of S-N compounds in solution.

The results of this literature survey, presented in Figure 1, are useful as a starting point in the discussion of S-N chemistry. Note, however, that not all of the reactions shown in Figure 1 actually proceed at any significant rate in FGD systems. The key points from Figure 1 are summarized below:

- Hydroxylamine disulfonic acid (HADS) is the first stable S-N compound formed in solution and results from a reaction between nitrite (NO_2^-) and bisulfite (HSO_3^-). In FGD systems, bisulfite is present through SO_2 absorption while nitrite forms as a result of NO_x absorption.

- HADS, once formed, can undergo a number of reactions including hydrolysis to other mono-negative nitrogen compounds such as hydroxylamine sulfonic acid (HAMS) and hydroxylamine, and sulfonation to tri-negative nitrogen compounds such as amine trisulfonic acid (ATS), amine disulfonic acid (ADS), and sulfamic acid. The tri-negative compounds can also hydrolyze with the final product being ammonia.

- Additional reactions are known in which nitrite can react with either the mono- or tri-negative nitrogen compounds. Reactions between nitrite and the tri-negative nitrogen compounds produce nitrogen (N_2) as a product while reactions between nitrite and the mono-negative nitrogen compounds can product products including various nitroso- compounds, nitric oxide (NO), and dinitrogen oxide (N_2O). no evidence has been found in this study that these reactions are significant.

Figure 1 shows that the beginning of the S-N chain is the reaction of nitrite and bisulfite to form HADS. In practice, however, these reactants must be formed from species removed from the flue gas. It is this step, specifically the removal of NO_x from the flue gas to form nitrite, which determines the overall rate of S-N formation. Several reactions have been identified which enhance NO_x removal and produce nitrite as a reaction product. Since these reactions can be affected by process operating conditions, the formation rate of S-N compounds is, in turn, a function of process operating conditions.

One aspect of the S-N question which was not investigated in this program is the potential toxicity of these compounds. Hydroxylamine, shown in Figure 1, is known to be toxic. However, this compound has not been found in the Arapahoe samples and is not expected to form at appreciable concentrations unless extremely acidic conditions exist. The toxicity of the other S-N compounds is not known. Toxicity testing is planned, however, pending the outcome of analyses on slurry from full-scale systems. These analyses are in progress and will help determine the identify and concentration of S-N species in FGD systems. The results of this investigation will be used to help focus the toxicity testing efforts.

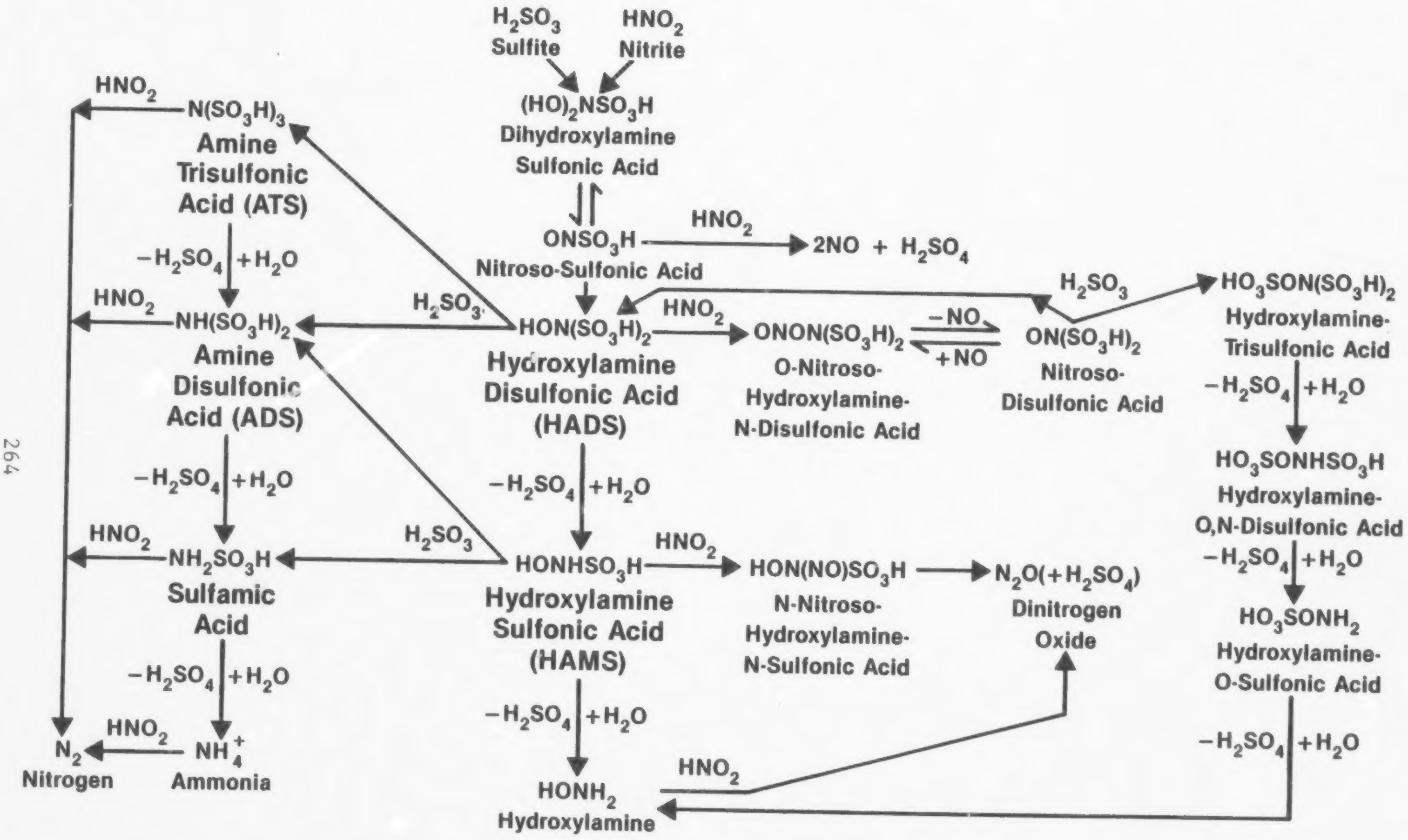

H_2SO_3
Sulfite
HNO_2
Nitrite
$(HO)_2NSO_3H$
Dihydroxylamine
Sulfonic Acid
$ONSO_3H$
Nitroso-Sulfonic Acid
HNO_2
$2NO + H_2SO_4$
HNO_2
$N(SO_3H)_3$
Amine
Trisulfonic
Acid (ATS)
$-H_2SO_4$
$+H_2O$
HNO_2
$NH(SO_3H)_2$
Amine
Disulfonic
Acid (ADS)
H_2SO_3
$HON(SO_3H)_2$
Hydroxylamine
Disulfonic Acid
(HADS)
HNO_2
$ONON(SO_3H)_2$
O-Nitroso-
Hydroxylamine-
N-Disulfonic Acid
$-NO$
$+NO$
$ON(SO_3H)_2$
Nitroso-
Disulfonic Acid
H_2SO_3
$HO_3SON(SO_3H)_2$
Hydroxylamine-
Trisulfonic Acid
$-H_2SO_4$
$+H_2O$
$HO_3SONHSO_3H$
Hydroxylamine-
O,N-Disulfonic Acid
$-H_2SO_4$
$+H_2O$
HO_3SONH_2
Hydroxylamine-
O-Sulfonic Acid
$-H_2SO_4$
$+H_2O$
$-H_2SO_4$
$+H_2O$
$-H_2SO_4$
$+H_2O$
HNO_2
NH_2SO_3H
Sulfamic
Acid
H_2SO_3
$HONHSO_3H$
Hydroxylamine
Sulfonic Acid
(HAMS)
HNO_2
$HON(NO)SO_3H$
N-Nitroso-
Hydroxylamine-
N-Sulfonic Acid
$N_2O(+H_2SO_4)$
Dinitrogen
Oxide
$-H_2SO_4$
$+H_2O$
$-H_2SO_4$
$+H_2O$
HNO_2
N_2
Nitrogen
NH_4^+
Ammonia
HNO_2
$HONH_2$
Hydroxylamine

Figure 1. Overall Sulfur-Nitrogen Reaction Scheme.

PRESENTATION OF RESULTS

The results of this test program are described in two sections. The first section describes the effect of process operating conditions on S-N formation and includes topics such as NO_x removal, HADS formation and decomposition, speciation of the S-N compounds formed during the Arapahoe tests, and factors affecting the concentrations of S-N compounds present under steady-state conditions. The second section describes the effect of S-N compounds on important operating characteristics such as SO_2 removal, system chemistry, pH, and solids oxidation and crystal structure.

THE EFFECT OF PROCESS OPERATING CONDITIONS ON S-N COMPOUND FORMATION

Sulfur-nitrogen compound formation is a stepwise process involving absorption of various nitrogen oxides to form nitrite, reaction of nitrite and bisulfite to form hydroxylamine disulfonic acid (HADS), and the hydrolysis and/or sulfonation of HADS to form other S-N compounds. The absorption of nitrogen oxides from the flue gas appears to be the rate limiting step in the formation sequence. That is, the formation rate of S-N compounds is determined by the rate of NO_x removal rather than the reaction between nitrite and bisulfite to form HADS. Therefore, an examination of how process conditions can affect NO_x removal is a good starting point for this discussion of S-N chemistry.

FACTORS AFFECTING NO_x REMOVAL

Both NO_2 and NO are relatively insoluble gases. If NO_x removal was entirely determined by gas solubility, NO_x mass-transfer would be extremely low. Higher NO_x mass-transfer rates are actually observed because of reactions which remove the dissolved gases from the liquid mass-transfer film. Four reactions have been identified which may enhance NO_x mass transfer:

$$2NO_2(aq) + H_2O \rightleftharpoons HNO_2 + H^+ + NO_3^- \qquad \text{(Reaction 1)}$$

$$NO(aq) + NO_2(aq) + H_2O \rightleftharpoons 2HNO_2 \qquad \text{(Reaction 2)}$$

$$NO_2(aq) + SO_3^{=} \rightleftharpoons NO_2^- + \text{products } (S_2O_6^{=},\ SO_4^{=}) \qquad \text{(Reaction 3)}$$

$$NO_2(aq) + HSO_3^- \rightleftharpoons NO_2^- + \text{products } (S_2O_6^{=},\ SO_4^{=}) \qquad \text{(Reaction 4)}$$

All four of these reactions help to increase the NO_x mass-transfer rate. However, the relative contribution of each depends on process conditions. Each of these reactions produces nitrite as a product which can react with bisulfite to form S-N compounds.

Reaction 1 involves disporportionation of NO_2. Note that nitrate is a by-product of this reaction along with nitrite. Reaction 2 involves the direct reaction of NO and NO_2. This reaction, however, produces no characteristic by-product such as the nitrate formed in Reaction 1. Reactions 3 and 4 involve the direct reaction of NO_2 with either sulfite or bisulfite, respectively. These reactions produce dithionate ($S_2O_6^{=}$) as a characteristic by-product. The mechanism of these reactions, however, are not well understood and other by-products such as sulfate have been reported (1).

From published kinetic data, both Reactions 1 and 2 should occur in FGD systems (2). However, the results of this study indicate that Reaction 1 is the more important of the two. This conclusion is based on the appearance of nitrate which is a characteristic by-product of Reaction 1. In the Arapahoe tests, sufficient nitrate was formed to account for, on the average, about two-thirds of the S-N compounds formed in the system.

Both Reactions 1 and 2 are far from equilibrium under scrubber conditions and the forward reactions are essentially irreversible. Therefore, the rate of nitrite formation due to these reactions is independent of the concentrations of reaction products in solution. Further, since no liquid phase species (other than the dissolved gases) are involved in the reaction, the rate of NO_x uptake is largely independent of slurry composition. This implies that the rate of NO_x uptake from these reactions should be constant for a given physical configuration (L/G ratio, NO_x concentration, and temperature).

By contrast, the rate of NO_2 uptake due to Reactions 3 and 4 is strongly dependent on slurry composition because sulfite and bisulfite are directly involved in the absorption reactions. Results from the laboratory and Arapahoe tests show that a considerable increase in the NO_2 mass transfer rate (and the S-N formation rate) occurs when the concentrations of sulfite and bisulfite are high.

Laboratory test results indicate that Reaction 3 (with sulfite) is much faster than Reaction 4 (with bisulfite). However, at the low pH conditions near the gas/liquid interface where these reactions take place, the bisulfite concentration is much higher than the sulfite concentration and both reactions contribute to NO_2 removal, nitrite formation, and S-N compound formation.

Test results from Arapahoe showed that under typical baseline conditions (limestone, pH 6, natural oxidation), Reactions 3 and 4 accounted for less than one-third of the S-N compound formation. However, when the dissolved sulfite/bisulfite concentration was high (e.g., in the high magnesium and low pH tests), high S-N formation rates were observed and direct reaction with sulfite/bisulfite was the predominant mechanism for NO_x removal.

The NO_2 removal efficiency could not be measured directly by gas phase analysis during the Arapahoe tests. This was the result of variability in the inlet gas concentrations of NO and NO_2, and the extremely low level of NO_x removed from the flue gas (an NO_x removal rate of only 3 ppm would account for the highest observed formation rate of nitrogen compounds in the system). Therefore, it is impossible to demonstrate a direct effect of dissolved sulfite on NO_x removal efficiency at Arapahoe. However, the effect of sulfite can be seen on the formation rate of S-N compounds in the system. This indirect evidence of the effect of sulfite on the rate of NO_x removal is shown in Figure 2. Supporting data, including a list of test conditions, is given in Table 1. Figure 2 shows the S-N formation rate

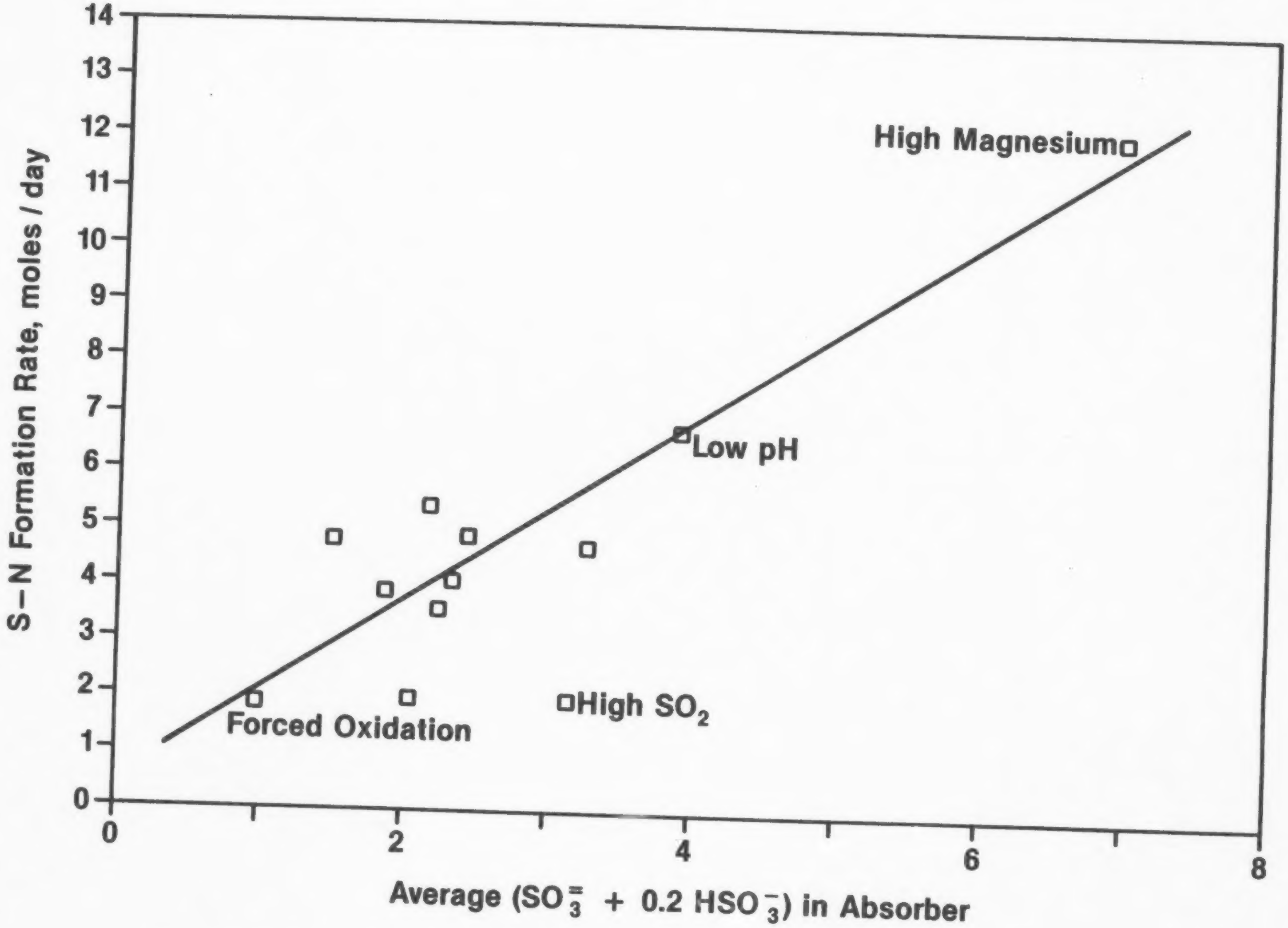


Figure 2. Arapahoe S-N Formation Rates vs. Absorber Sulfite Concentration.

TABLE 1. MEASURED S-N FORMATION RATES AT ARAPAHOE AS A FUNCTION OF PROCESS CONDITIONS

Test	Measured S-N Formation Rate, moles/day	Process Conditions
First Baseline	3.9	Baseline[1]
Low pH	7.4	pH = 5.2
Mid pH	4.7	pH = 5.7
High L/G	4.9	4 spray nozzles
Second Baseline	4.2	Baseline
High SO_2	2.2	SO_2 = 2000 ppm
High Mg^{+2}, Natural Oxid.	12.0	Mg^{+2} = 150 mmoles/l
High Mg^{+2}, Forced Oxid.	4.4	Mg^{+2} = 150 mmoles/l
Third Baseline	5.4	Baseline
Forced Oxidation	1.6	Low Mg^{+2}
Lime	1.0	pH = 7; service water
Lime	1.9	pH = 7; CTB water

[1] Baseline conditions are: pH = 6.2, inlet SO_2 = 500 ppm, natural oxidation; Mg^{+2} < 30 mmoles/l; L/G = 45 Gal/macf (2 nozzles)

measured by mass balance at Arapahoe versus an empirical correlation involving the dissolved sulfite/bisulfite concentrations within the absorber. These results show that the measured S-N formation rate increased as the dissolved sulfite/busulfite concentrations in the absorber increased. The lowest S-N formation rate occurred in the forced oxidation test where dissolved sulfite/bisulfite was low. The highest S-N formation rate occurred in the high magnesium test where dissolved sulfite/bisulfite was high. A relatively high S-N formation rate was also measured in the low pH test where the bisulfite concentration was quite high.

The S-N formation rates shown in Figure 2 and Table 1 were determined by mass balance calculations. The procedure consisted of measuring the change in the inventories of these compounds in the system with time and accounting for the discharge of these compounds from the system in the filter cake. In all, twelve individual tests were conducted with each test lasting from 7 to 10 days.

The S-N formation rates in Figure 2 are plotted against an empirical correlation involving the average sulfite and bisulfite concentrations of the liquid within the absorber. The coefficient for the bisulfite term (0.2) was determined from a best fit of the experimental data and represents, to some degree, the relative reaction rates of NO_2 with sulfite and bisulfite. The same coefficient for the bisulfite term also gave the best fit for a similar test matrix performed in the laboratory.

The use of the average sulfite and bisulfite concentrations in the absorber represents a practical means of displaying the Arapahoe results since these quantities were either measured directly or calculated using the Radian Species Distribution Program. However, it should be noted that the reactions which promote NO_x removal actually occur at the gas/liquid interface where the pH is lower and the sulfite/bisulfite concentrations are much different than in the bulk absorber liquid. Unfortunately, the conditions at the gas/liquid interface are difficult to determine without a sophisticated mass-transfer model. Further, these variables change as a function of position within the absorber. Even with this limitation, however, the data in Figure 2 still indicate the important effect of dissolved sulfite/bisulfite on the formation rate of S-N compounds.

Variation in the liquid interface pH may explain why the result for the high inlet SO_2 point falls below the indicated correlation in Figure 2. In this case, the higher SO_2 mass-transfer rate depresses the liquid interface pH relative to the remainder of the tests at the lower inlet SO_2 level. This shifts the sulfite/bisulfite equilibrium toward bisulfite and decreases the NO_2 absorption efficiency. It should also be noted that the L/G ratio was not increased in this test to compensate for the increased inlet SO_2 level. Had this been done, the S-N formation rate would almost certainly have been higher.

FORMATION OF HADS

As shown in Figure 1, HADS is the first stable S-N compound formed in solution. During the formation process (from nitrite and bisulfite), nitrogen is reduced from a valence of +3 to -1 while sulfur is oxidized from a valence of +4 to +6.

The kinetics of this reaction have been characterized and are believed to follow a rate expression of form (3):

$$\frac{d[HADS]}{dt} = k_1[H^+]^2[NO_2^-] + k_2[H^+][NO_2^-][HSO_3^-] + k_3[NO_2^-[[HSO_3^-]^2 \qquad \text{(Equation 1)}$$

where: $k_1 = 8 \times 10^5 \ (L^2/mole^2 \cdot s)$

$K_2 = 3.7 \times 10^{12} \ e^{-6100/T} \ (L^2/mole^2 \cdot s)$

$K_3 = 9.0 \times 10^{-4} \ e^{2.1\sqrt{u}} \ (L^2/mole^2 \cdot s)$

T = Temperature (°K)

u = Ionic strength (moles/1)

At typical scrubber conditions, the second term in Equation 1 dominates and the reaction rate is first order with respect to the concentrations of hydrogen ion, nitrite, and bisulfite.

Equation 1 can be used to estimate the concentration of nitrite present under steady-state conditions. For the baseline case (limestone, pH 6, natural oxidation), the nitrite concentration estimated from Equation 1 is about 10^{-4} M. This low value for the nitrite concentration is consistant with the experimental results at Arapahoe where the nitrite concentration was generally too low for direct measurement by ion chromatography.

FORMATION OF OTHER S-N COMPOUNDS

HADS, once formed, can react to form other S-N compounds. At least three mechanisms are known by which this can occur. These include:

1) Hydrolysis of many of the S-N compounds. For the mono-negative nitrogen compounds, the hydrolysis reaction follows the pathway;

   HADS ⟶ HAMS ⟶ Hydroxylamine

   For the tri-negative nitrogen compounds, the hydrolysis reaction follows the pathway;

   ATS ⟶ ADS ⟶ Sulfamic Acid ⟶ Ammonia

2) Sulfonation of the mono-negative nitrogen compounds (HADS, HAMS) to tri-negative nitrogen compounds (ADS, sulfamic acid).

3) Reaction between nitrite and some of the S-N compounds. The mono-negative nitrogen compounds react with nitrite to form various nitroso- compounds, NO and N_2O. The tri-negative nitrogen compounds react with nitrite to form nitrogen.

Laboratory tests were performed to determine the stability of S-N compounds with respect to the above reactions. The objectives of these tests were to learn more about the chemistry of S-N compounds and to develop techniques to stabilize scrubber samples for later analysis. The results of these experiements are summarized below:

- HADS is readily hydrolyzed to HAMS under scrubber conditions. The reaction proceeds more rapidly at lower pH levels. HAMS, however, is relatively stable with respect to hydrolysis and prolonged boiler under acidic conditions is required to hydrolyze HAMS to hydroxylamine. Therefore, hydroxylamine is not expected to be present at significant concentrations in scrubbers.

- Both HADS and HAMS can be readily sulfonated in scrubbers because an excess of bisulfite is usually present. This reaction is dependent on the concentrations of both the S-N compounds and bisulfite, and proceeds more rapidly at lower pH. The sulfonation of HADS yields a mixture of ATS and ADS. However, ATS immediately hydrolyzes to ADS. At the baseline conditions used in the Arapahoe tests, sulfonation of HADS to ADS was the predominant decomposition pathway (as opposed to hydrolysis). HAMS, if formed by HADS hydrolysis, can also be sulfonated. Here, the products include ADS and sulfamic acid.

- Reaction between nitrite and the mono- and tri-negative nitrogen S-N compounds can also occur. However, the concentrations of nitrite and the S-N reactants are so low that these reactions are not thought to be significant. No evidence has been found in this study that nitroso- compounds are present in significant levels in FGD systems.

The decomposition test results indicate that under typical scrubber conditions, the S-N compounds that will be present in solution include ADS, HADS, HAMS, and sulfamic acid. ADS is expected to be present at the highest concentration under natural oxidation conditions where bisulfite is present. When bisulfite is low (e.g., forced oxidation or high pH), HADS or HAMS might be expected as the predominant S-N compounds. In the next section, speciation results from the Arapahoe tests are presented. The results of these analyses are consistent with the results of the decomposition tests.

SPECIATION OF THE ARAPAHOE SAMPLES FOR S-N COMPOUNDS

Samples were taken near the end of each of the twelve tests conducted at Arapahoe. These samples were analyzed for S-N and related compounds by the methods listed below:

HADS, ADS, $S_2O_6^=$	Ion chromatography-strong eluent
$SO_4^=$, NO_3^-	Ion chromatography-normal eluent
F^-, sulfamate, Cl^-	Ion chromatography-weak eluent
$SO_3^=$	Iodimetric titration
Ammonia	Ammonia distillation
Hydroxylamine	Thin-layer chromatography (semi-quantitative)
Total sulfur	Acid hydrolysis, ion chromatography-normal eluent
Total mono-negative nitrogen	Acid hydrolysis, permanganate titration
HAMS	By difference (total mono-negative nitrogen - HADS
Total nitrogen	Acid hydrolysis, Devarda's reduction, ammonia distillation

The speciation results from the Arapahoe samples are shown in Table 2. These results show that the most common S-N compounds in solution include HADS, ADS, and HAMS. Trace amounts of sulfamic acid and ammonia were also found. However, no hydroxylamine was measured (at a detection limit of 0.3 ppm).

The data in Table 2 was used in conjunction with other analytical and process data to perform mass balances on the Arapahoe pilot system. This procedure, used previously to determine the S-N formation rate, is also useful in identifying decomposition pathways. The results of this analysis are summarized below:

- HADS sulfonation, rather than hydrolysis, was the major decomposition pathway in the Arapahoe tests. In this pathway, HADS sulfonates to ADS and ATS (ATS then hydrolyzes to ADS). Note that an alternate pathway could be hydrolysis of HADS to HAMS followed by sulfonation of HAMS to ADS and sulfamic acid. However, the low concentration of sulfamic acid in solution indicates that this is probably not a significant pathway.

TABLE 2. SPECIATION RESULTS FOR ARAPAHOE TEST SAMPLES

Test [1]	ADS, mm/L	HADS, mm/L	HAMS, [2] mm/L	SA, mm/L	NO_3^-, mm/L	NH_4^+, mm/L	$S_2O_6^=$, mm/L	$SO_4^=$ [3], mm/L	Total Sulfur, mm/L	Total Hydrolyzed Nitrogen, mm/L
First Baseline [4]	1.5	0.70	0.67	<0.1	1.6	—	—	34.0	38.4	—
Low pH [4]	3.5	0.23	1.5	<0.1	2.9	—	—	40.1	50.4	—
Mid pH	4.1	0.50	0.6	<0.1	4.2	1.9 [5]	2.7	33.8	50.7	12.0
High L/G	4.3	1.0	0.3	<0.1	5.2	1.5 [5]	2.7	34.7	55.0	12.4
Second Baseline	4.8	1.1	1.0	<0.1	4.8	1.5 [5]	1.9	42.7	60.8	13.4
High SO_2	2.3	0.4	2.8	<0.1	3.8	0.2	1.2	45.7	62.2	8.1
High Mg^{+2}, Natural Oxid.	4.3	0.7	3.6	<0.1	3.5	0.2	1.2	156	170	10.6
High Mg^{+2}, Forced Oxid.	5.4	0.7	3.3	<0.1	4.2	0.3	1.8	165	199	12.9
Third Baseline	0.9	0.7	1.4	<0.1	1.5	0.2	<0.2	45.4	50.6	4.0
Forced Oxidation	1.1	0.5	0.8	<0.1	1.8	0.2	0.4	46.1	47.7	4.1
Lime (Service Water)	1.5	1.5	0.8	<0.1	2.9	0.1	0.6	54.3	55.9	5.3
Lime (CTB Water)	1.2	1.1	0.5	<0.1	4.0	0.2	0.5	61.5	72.3	6.0

[1] All analyses measured at the end of the test specified.

[2] HAMS by difference: Total mononegative nitrogen - HADS.

[3] $SO_4^=$ value listed here includes sulfite species.

[4] Field analyses.

[5] These values appear to be high relative to the remainder of the data set.

- Under most conditions, ADS becomes the most concentrated S-N compound in solution because it is relatively stable under scrubber conditions. Under some conditions (low pH and/or high bisulfite), almost no HADS would be present at steady-state. By contrast, HADS would become the most concentrated S-N compound under conditions such as forced oxidation or high pH (>7) where bisulfite is low.

Table 2 also shows that significant amounts of both nitrite and dithionate were found in samples from Arapahoe. Both of these compounds are believed to have formed as a result of the reactions responsible for NO_x removal. No other sources were identified for either of these compounds although dithionate may be involved as an intermediate in the sulfite oxidation mechanism.

In addition to the analyses for individual compounds, analyses were also performed for total sulfur and total nitrogen. These analyses were compared to the sum of the individual analyses to determine whether or not all of the sulfur and nitrogen compounds in solution were accounted for. The results for the total sulfur comparison were very good. The value measured for total sulfur was within +10% of the summation of individual sulfur species for all of the samples shown in Table 2. This is a good indication that most of the sulfur species present in solution have been identified.

Total nitrogen balances were also performed. The results of this comparison showed that the value for the total nitrogen analysis was, on the average, about 9 percent below the summation of individual nitrogen species. This bias is probably due to incomplete recovery of nitrogen during the total nitrogen analysis. The total nitrogen analysis used for these samples involved acid hydrolysis followed by reduction of nitrogen species to ammonia. During the hydrolysis step, some of the hydroxylamine formed by hydrolysis of the tri-negative nitrogen species may be lost as N_2O. Work is continuing on the development of a total nitrogen procedure that will provide complete recovery of all nitrogen species.

STEADY-STATE CONCENTRATIONS OF S-N COMPOUNDS IN SCRUBBER SYSTEMS

The final topic in this section concerns the steady-state concentrations of S-N compounds which can be expected to accummulate in scrubber systems. This is important because the effects of S-N compounds on scrubber operation (discussed in the next section) are largely functions of their concentration in the system.

From data taken during the Arapahoe pilot tests, estimates were prepared for the steady-state concentration of S-N compounds as a function of process operating conditions. Estimates of these values are required because the 7 to 10 day test period at each set of operating conditions was not nearly long enough to establish steady-state concentration profiles in the system (one liquid phase residence time under baseline closed-loop conditions at Arapahoe is approximately two months).

The steady-state S-N concentration is a function of two factors. These are the S-N formation rate and the liquid blowdown rate. In the Arapahoe tests, the S-N formation rate was measured at each set of test conditions. The liquid blowdown rate was computed using average values for the solids production rate and the weight percent solids in the filter cake.

The estimated steady-state S-N concentrations for each of the tests at Arapahoe are shown in Table 3 along with the S-N formation rate measured in each test. The results show that the concentration of S-N compounds would have been expected to remain under 23 mmoles/l for realistic test conditions (excluding the low pH test). This relatively low level of S-N compounds is the result of the extremely low NO_x removal efficiency. Even at conditions which resulted in the highest S-N formation rate, the NO_x removal required to form the S-N compounds was only 2 to 3 ppm from the flue gas. At an inlet NO_x concentration which averaged about 600 ppm, this represented an NO_x removal efficiency of only 0.5 percent.

The highest S-N concentration would be expected in the high magnesium-natural oxidation test. This is the result of the high S-N formation rate which, in turn, was caused by the higher concentration of dissolved sulfite present under these test conditions. The lowest S-N concentration was expected for the high SO_2 test. This test, conducted at an inlet SO_2 concentration of 2000 ppm, gave an estimate for the S-N concentration of only 1.2 mmoles/l. This result reflects the general effect of increasing the inlet SO_2 concentration. For a given system, increasing the inlet SO_2 level increases the SO_2 pickup per pass. However, since the inlet NO_x concentration remains unchanged, the ratio of the sulfur to nitrogen removed from the flue gas increases, even if the L/G ratio is increased to maintain high SO_2 removal. This change in the sulfur to nitrogen ratio removed from the flue gas must be reflected in the concentrations of these elements in the slurry and the net effect is a decrease in the S-N compound concentration.

There are other factors which can also contribute to a lower concentration of S-N compounds in high SO_2 systems. These include a decrease in the gas/liquid interface pH and a decrease in solid phase oxidation. Lower interface pH levels occur due to the higher SO_2 mass transfer rates across the interface. Therefore, the sulfite/bisulfite shift will favor bisulfite which decreases the rate of NO_x mass transfer (relative to sulfite). Decreased oxidation of the solid phase is another effect of increasing the inlet SO_2 concentration. Lower oxidation solids do not generally dewater as efficiently as higher oxidation solids. Higher water losses decrease the cycles of concentration and further reduce the level of S-N compounds in solution.

It should be pointed out that there are operating conditions which may lead to much higher concentrations of S-N compounds than are estimated from the Arapahoe results. These conditions occur in dual alkali systems in which the dissolved sulfite concentration can be extremely high. Washing of the filter cake to minimize sodium losses would serve to further concentrate S-N compounds.

TABLE 3. ESTIMATED STEADY-STATE S-N CONCENTRATIONS FROM THE ARAPAHOE TESTS AS A FUNCITON OF PROCESS CONDITIONS

Test	Measured S-N Formation Rate, moles/day	Estimated Steady-State S-N Concentration, mmoles/l
First Baseline	3.9	7.1
Low pH	7.4	26.4
Mid pH	4.7	14.6
High L/G	4.9	12.7
Second Baseline	4.2	10.5
High SO_2	2.2	1.2
High Mg^{+2}, Natural Oxid.	12.0	22.6
High Mg^{+2}, Forced Oxid.	4.4	14.2
Third Baseline	5.4	11.1
Forced Oxidation	1.6	11.4
Lime	1.0	3 - 4
Lime	1.9	6 - 7

THE EFFECT OF S-N COMPOUNDS ON FGD SYSTEM PERFORMANCE

The absorption of acidic species such as NO_2 and HCl causes several changes in FGD process chemistry. For example, the absorption of HCl, produced during the combustion of high chloride coal, results in an increase in the concentration of calcium chloride through the following reaction:

$$CaCO_3 + 2HCl \rightleftharpoons Ca^{+2} + 2Cl^- + CO_2\uparrow + H_2O \qquad \text{(Reaction 5)}$$

The increase in the calcium chloride concentration has two effects. First, higher calcium shifts the equilibrium in Reaction 5 to the left. This increases the hydrogen ion concentration and decreases reaction tank pH at constant limestone reagent ratio. Second, increased calcium decreases the concentrations of alkaline species such as sulfite and carbonate through solubility effects. These factors are partially responsible for the decreases in SO_2 removal associated with calcium chloride accumulation (4,5).

The situation with NO_2 absorption is entirely analogous to that for HCl except that instead of chloride, the anions which accumualte in solution include $HADS^=$, $ADS^=$, $HAMS^-$, sulfamate, NO_2^-, NO_3^-, and $S_2O_6^=$. Once again, the calcium concentration increases as needed to balance these anions in solution. There is one significant difference, however, between absorption of NO_2 and HCl. Removal of HCl in the absorber is usually high since HCl is very soluble, whereas, removal of NO_2 is low. Chloride concentrations above 1000 mmoles/l are possible in full-scale FGD systems treating flue gas from high chloride coal (5). Since S-N accumulation is only on the order of 25 mmoles/l and lower (not including NO_2^-, NO_3^-, or $S_2O_6^=$), the potential for adverse effects on SO_2 removal is much lower.

Laboratory tests were conducted on Radian's bench-scale FGD system to evaluate the effect of S-N accumulation (high calcium) on SO_2 removal and operating pH. These tests were conducted over a wide pH range at S-N concentrations up to 50 mmoles/l. This S-N level was selected to represent an upper bound on the concentrations of S-N compounds likely to accumulate in full-scale systems. The test results, evaluated at constant limestone reagent ratio, showed that operating pH decreased about 0.5 units at the 50 mmoles/l S-N level. However, SO_2 removal fell by only 3 to 4 percent. The drop in pH caused by an increase in the concentrations of calcium and S-N related compounds does not have as severe an effect on SO_2 removal as the pH drop associated with a decrease in the limestone reagent ratio. The latter generally results in more significant changes in SO_2 removal. Both the decrease in operating pH and the observed effect on SO_2 removal are roughly in agreement with test results for chloride at equivalent concentration levels. Therefore, S-N compounds should not be a major cause for concern with respect to SO_2 removal in most systems.

There are, however, some cases in which the increase in calcium associated with S-N formation could have a more significant effect on FGD system operation. For example, relatively high levels of S-N compounds are expected in systems using magnesium to improve SO_2 removal. In these systems, extra magnesium is required to reduce the calcium concentration and offset the adverse effects of S-N and related compounds. A typical reaction (assuming addition of $MgSO_4$) would be:

$$Ca^{+2} + HADS^{=} + MgSO_4 \rightleftharpoons CaSO_4\downarrow + Mg^{+2} + HADS^{=} \quad \text{(Reaction 6)}$$

Once the concentration of calcium is reduced, the sulfite concentration can rise and help promote SO_2 removal.

In the Arapahoe test with magnesium, the steady-state S-N concentration was estimated at 23 mmoles/l. Using reasonable assumptions on the distribution of species at this S-N level, the estimated concentration of all S-N related anions would be about 80 meq/L ($HADS^{=}$, $ADS^{=}$, $HAMS^{-}$, sulfamate, NO_3^{-}, NO_2^{-}, and $S_2O_6^{=}$). In this example, an additional 80 meq/L (970 ppm) of extra magnesium would be required to offset the S-N related species in solution. This directly increases operating costs.

Tests were also conducted at Arapahoe to evaluate the effect of S-N compounds on SO_2 removal and pH. However, even after six weeks of operation, the S-N concentration increased to a level of only 7 mmoles/l. At this concentration, no clear effects of S-N compounds were observed on either SO_2 removal or operating pH.

The effect of S-N compounds on solid waste properties such as oxidation level and crystal morphology was evaluated in both the laboratory and Arapahoe tests. The only significant effect of S-N compounds was seen in laboratory tests in which HADS appeared to act as an inhibitor in the oxidation of sulfite. However, the tests showing this effect were limited in scope. Since oxidation is an important variable in the operation of FGD systems, this effect warrants further investigation.

CONCLUSIONS

1. The S-N compounds found in solution include HADS, HAMS, ADS, and sulfamic acid. No evidence was found for the presence of hydroxylamine or nitroso- compounds.

2. The rate limiting step in S-N formation is absorption of NO_x from the flue gas. Variables which affect NO_x removal include the absorber mass-transfer characteristics (L/G ratio, contactor design, etc.), the gas phase NO_x concentration, and the sulfite/bisulfite concentration at the gas/liquid interface. Process operating conditions can affect the sulfite concentration and, therefore, the formation rate of S-N compounds. The highest formation rates of S-N compounds were observed under conditions which promoted high concentrations of dissolved sulfite/bisulfite.

3. The concentration of S-N compounds in FGD systems is a function of both the S-N formation rate and the liquid blowdown rate. The latter is a function of the solids production rate and the efficiency of the dewatering system. The Arapahoe results indicate tha the concentration of S-N compounds expected in typical systems should remain below 20

mmoles/l. However, higher levels may be found in low inlet SO_2 systems and systems with high concentrations of dissolved sulfite/bisulfite.

4. S-N compounds have an effect on FGD operation similar to that of HCl absorption. The effect, which is actually caused by elevated calcium concentrations, results in a decrease in operating pH, a decrease in the concentrations of alkaline sulfite and carbonate, and a decrease in SO_2 removal. At the S-N concentrations expected in most FGD systems (<20 mmoles/l), these effects should not significantly impair FGD operation. However, if present at higher levels, S-N compounds could result in measureable decreases in SO_2 removal.

5. S-N compounds may cause inhibited sulfite oxidation. The results of this program, however, are inconclusive and further investigation is warrented.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

REFERENCES

1. Sato, T., Matani, S., and Okabe, T. The Oxidation of Sodium Sulfite with Nitrogen Dioxide. Paper presented at the National Meeting of the American Chemical Society, Honolulu, Hawaii, April 1, 1979.

2. Schwartx, S.E., and White, W.H., Kinetics of Reactive Dissolution of Nitrogen Oxides into Aqueous Solution. In: S.E. Schwartz (ed.), "Trace Atmospheric Constituents, Properties, Transformations, and Fotes." John Wiley and Sons. New York, New York 1983, pp 1-116.

3. Oblath, S.B., Markowitz, S.S., Novakov, T., and Chang, S.G., Kinetics of the Formation of Hydroxylamine Disulfonate by Reaction of Nitrite with Sulfites. The Journal of Physical Chemistry, 85: pp 1017-1021, 1981.

4. Jarvis, J.B., Trofe, T.W., and Stewart, D.A., Effect of High Dissolved Solids on Bench-Scale FGD Performance. Paper presented at the EPA/EPRI Symposium on Flue Gas Desulfurization. New Orleans, Louisiana, November 1-4, 1983.

5. Downs, W., Johnson, D.W., Aldred, R.W., Tontz, L.V., Robards, R.F., and Runyan, R.A., Influence of Chlorides on the Performance of Flue Gas Desulfurization. Paper presented at the EPA/EPRI Symposium on Flue Gas Desulfurization. New Orleans, Louisiana, November 1-4, 1983.

THIOSULFATE AS AN OXIDATION INHIBITOR IN FLUE GAS DESULFURIZATION PROCESSES: A REVIEW OF R&D RESULTS

by: Gary T. Rochelle and David R. Owens
The University of Texas at Austin
Austin, TX 78712

John C. S. Chang
Acurex Corporation
Research Triangle Park, NC 27709

Theodore G. Brna
U. S. Environmental Protection Agency
Air and Energy Engineering Research Laboratory
Research Triangle Park, NC 27711

ABSTRACT

Sodium thiosulfate ($Na_2S_2O_3$) has been tested in a pilot plant as an oxidation inhibitor in flue gas desulfurization by lime and limestone slurry scrubbing with and without MgO and adipic acid additives. The effectiveness of thiosulfate is proportional to the inhibitor product, defined as the product of thiosulfate concentration(M), calcium concentration(M), and the moles of SO_2 absorbed per hour per liter of hold tank volume. Gypsum saturation was less than 100% and scaling was eliminated when the inhibitor product exceeded 0.3×10^{-6} M^3/hr. Thiosulfate was relatively more effective in systems with chlorides and less effective in systems promoted by MgO. An inhibitor product greater than 10^{-6} M^3/hr significantly enhanced dewatering of solids from limestone scrubbing. SO_2 removal and/or limestone utilization were increased in systems that started with less than 10 mM dissolved calcium.

This paper has been reviewed in accordance with the U. S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

Sulfite oxidation is an important side reaction in flue gas desulfurization processes using aqueous solutions. In slurry scrubbers using lime or limestone, gypsum ($CaSO_4 \cdot 2H_2O$) scaling on scrubber internals and mist eliminators has in many cases been a serious reliability problem. Thiosulfate ($S_2O_3^{=}$) has been identified and tested as an effective oxidation inhibitor in slurry scrubbing systems. It reduces gypsum saturation and thereby reduces scaling. It also enhances the dewatering properties of calcium sulfite solids, enhances SO_2 removal when used with MgO, and reduces oxidative degradation of organic acid additives.

This paper is a review of research and development results on thiosulfate as an oxidation inhibitor in flue gas desulfurization. New pilot plant results are also presented on the effectiveness of thiosulfate in five lime/limestone slurry scrubbing processes.

Table 1 is a chronological summary of the work on thiosulfate. Thiosulfate was recognized as an oxidation inhibitor in early work by the Tennessee Valley Authority (TVA)(1) and Fuji Electric Company(3). In 1978, Radian Corporation rediscovered it as the oxidation inhibitor present with carbide lime and responsible for the scale-free operation of a scrubber operated by Louisville Gas and Electric(4). Further development was slowed by negative results with lime scrubbing in the Environmental Protection Agency (EPA) pilot plant at Research Triangle Park (RTP)(5). Nevertheless, in 1979 Duquesne Light successfully started adding sodium thiosulfate to eliminate gypsum scaling and enhance SO_2 removal in a 387 MW scrubber system using magnesium-promoted lime(7).

Table 1: CHRONOLOGICAL SUMMARY OF WORK WITH THIOSULFATE

Date	Organization	Scale	Results
1972	TVA(1)	lab	7 mM(millimolar) thiosulfate stopped sulfite oxidation at pH 5
1972	Louisville Gas and Electric(2)	150 MW	Carbide lime at Paddy's Run gives low oxidation and scale-free operation
1974	Fuji Electric(3)	lab	Thiosulfate inhibits sodium sulfite oxidation (patent)
1977	Radian(4)	lab	Identifies thiosulfate as probable inhibitor at Paddy's Run
1978	EPA(5)	pilot	Thiosulfate appears ineffective with lime
1979	U. of Va.(6)	lab	0.2 mM thiosulfate practically stops oxidation at pH 4
1979	Duquesne(7)	pilot & 387 MW	0.002 mole thiosulfate/mole CaO stops scaling in MgO-promoted lime scrubber at Phillips station
1980	Duquesne(7)	494 MW	Thiosulfate used at Elrama station with MgO-promoted lime
1981	U. of Tx.(7,8,9)	lab	1 mM thiosulfate stops sulfite and organic acid oxidation
1981	Bechtel/TVA (10)	10 MW	10 mM thiosulfate inhibits oxidation and enhances dewatering in limestone scrubber but degrades
1981	Battelle(7)	lab	Confirm inhibition, review work to date
1982	TVA(11,12,13)	10 MW	In a limestone scrubber1 mM thiosulfate inhibits oxidation, >3 mM enhances solids dewatering
1982	Battelle(14)	lab	Primary degradation product is trithionate
1983	U. of Tx(15,16)	lab	Thiosulfate inhibits oxidation catalyzed by Mn better than by Fe
1984	U. of Tx(17,18)	lab	Inhibition quantified; thiosulfate degrades initially at 1 mM/hr
1984	Acurex/EPA(19)	pilot	Thiosulfate demonstrated to be effective with lime or limestone w or w/o DBA or MgO
1985	Peabody/ Seminole(20)	1240 MW	Thiosulfate eliminates scaling and enhances dewatering in limestone w and w/o DBA

In 1981, laboratory work at the University of Texas(8) demonstrated that as little as 1 millimolar(mM) thiosulfate would practically stop sulfite oxidation and adipic acid degradation at pH 5. One test at 10 mM thiosulfate with limestone slurry in the 10 MW spray scrubber at TVA's Shawnee Station drastically reduced sulfite oxidation and enhanced solids dewatering, but the thiosulfate appeared to degrade rapidly(10). In 1982 extensive testing at Shawnee(11) showed that thiosulfate was effective at 1 mM in reducing gypsum saturation and at 3 mM in enhancing dewatering of the waste solids. Battelle(14) identified trithionate as the primary thiosulfate degradation product. In 1983-84, laboratory work at the University of Texas quantified sulfite oxidation and thiosulfate degradation as a function of solution composition(17).

In 1983-84, extensive testing was performed in the EPA-RTP pilot plant in a turbulent contact absorber (7.5 m^3/min) with lime and limestone slurry with and without magnesium and organic acid additives. These results quantified the effect of thiosulfate on gypsum saturation and solids dewatering and demonstrated that thiosulfate addition is generally useful in any slurry scrubbing process not using forced oxidation. In this paper further analysis of these and previous results is given to quantify the effects of thiosulfate and the makeup requirements.

In 1985, use of thiosulfate was initiated by Seminole Electric Cooperative in its 1240 MW plant at Palatka, Florida(20). This system uses thiosulfate to eliminate gypsum scaling and enhance solids dewatering in a limestone slurry scrubber.

EFFECTS OF THIOSULFATE

Thiosulfate has been tested extensively in limestone slurry scrubbing at Shawnee and RTP. At RTP, additional testing has also been performed in limestone scrubbing promoted by MgO and by adipic acid and in lime scrubbing alone and promoted by MgO. These systems all had SO_2 inlet gas concentrations of 2000 to 3000 ppm.

Without thiosulfate, all of the processes operated with sulfite oxidation of 17 to 20% and gypsum saturation greater that 100%. Significant gypsum scaling was observed with lime and limestone alone and light scaling with addition of $MgSO_4$ or adipic acid. With the lowest maintainable thiosulfate concentration, 0.9 mM, all of the processes operated with less than 100% gypsum saturation and no gypsum scaling. At higher thiosulfate levels solids dewatering was enhanced using limestone with or without adipic acid, and SO_2 removal or limestone utilization was improved slightly in all of the processes except lime scrubbing. Thiosulfate was generally more effective in the limestone systems when chloride was present at higher levels.

SULFITE OXIDATION

The primary effect of thiosulfate is to inhibit sulfite oxidation. Laboratory measurements have established some trends in the effects of solution composition on the rate of sulfite oxidation. Pilot plant data from EPA-RTP and Shawnee include measurement of solids oxidation; however, the analytical precision is poor at low oxidation levels.

Thiosulfate appears to function as a free radical scavenger rather than a complexer of S(IV)(sulfite plus bisulfite) or metal ions.. Its effective concentration is much less than S(IV); therefore, it probably does not form an unoxidizable complex with S(IV). Using literature values for the chelating constant ($[\text{Fe chelate}]/([Fe^{+++}]\,[S_2O_3^{=}]) = 447\ M^{-1}$ (21)), only 50% of the Fe^{+++} should be chelated with 1 mM thiosulfate. Other metals are even less strongly chelated. Furthermore thiosulfate appears to degrade as it functions, consistent with a role as a free radical scavenger, but inconsistent with complexing.

A probable mechanism for S(IV) oxidation in the presence of thiosulfate includes some constant rate of free radical initiation catalyzed by Fe (r_i), a limiting propagation reaction such as,

$$SO_3^{=} + SO_4^{-\cdot} \longrightarrow SO_3^{-\cdot} + SO_4^{=} \qquad (1)$$

$$r_{ox} = k_{ox}[SO_3^{=}][SO_4^{-\cdot}] \qquad (2)$$

and a termination reaction limited by thiosulfate and giving tetrathionate.

$$S_2O_3^{=} + SO_4^{-\cdot} \longrightarrow S_2O_3^{-\cdot} + SO_4^{=} \qquad (3)$$

$$2S_2O_3^{-\cdot} \longrightarrow S_4O_6^{=} \qquad (4)$$

$$r_t = k_t[S_2O_3^{=}][SO_4^{-\cdot}] \qquad (5)$$

The thiosulfate radical has been studied by Hayon (22), and oxidation of thiosulfate by iodine or other oxidants typically gives tetrathionate(23). Assuming that r_i=r_t, this oxidation mechanism gives a rate equation of the form:

$$r_{ox} = (r_i k_{ox}/k_t)([SO_3^{=}]/[S_2O_3^{=}]) \qquad (6)$$

By substituting the equilibrium of sulfite and bisulfite and assuming that S(IV) is mostly bisulfite, valid for pH less than 6:

$$[SO_3^{=}] = K_a[HSO_3^{-}]/[H^+] = K_a[S(IV)]/[H^+] \qquad (7)$$

$$r_{ox} = (r_i k_{ox} K_a/k_t)([S_2O_3^{=}][H^+]/[S(IV)])^{-1} \qquad (8)$$

Because most of the solutions are approximately saturated with calcium sulfite, Eq. 6 can also be expressed in terms of Ca^{++} concentration by substitutung the solubility relationship:

$$[SO_3^{=}] = K_{sp}/[Ca^{++}] \qquad (9)$$

Using Ldg to represent the moles of SO_2 absorbed per hour per liter of hold tank volume(M/hr), the fraction oxidation, f_{ox}, is equal to r_{ox}/Ldg and is given by combining Eqs. 6 and 9:

$$f_{ox} = (r_i K_{sp} k_{ox}/k_t)/([Ca^{++}][S_2O_3^{=}]Ldg) \qquad (10)$$

where the product of calcium, thiosulfate, and loading is defined as the inhibitor product.

Owens(17) measured the rate of sulfite oxidation by air in a vigorously stirred solution of 0.3 M Na_2SO_4 at 50°C with pH 4.5 to 6, 3 to 30 mM S(IV) (total sulfite plus bisulfite), 0.1 to 9.5 mM sodium thiosulfate, and 0.001 to 0.05 mM Fe^{++}. When the ratio of thiosulfate to S(IV) is greater than 0.1, Figure 1 shows that his results are correlated by Eq. 8 with the coefficient given by:

$$r_i k_{ox} K_a/k_t = 10^{-9}\ M^2/hr \qquad (11)$$

The rate of oxidation is approximately independent of oxygen and Fe^{++} concentration, although the rate was much slower with no Fe^{++} added. Manganese (Mn^{++}) did not appear to be a catalyst in the presence of thiosulfate.

In a slurry scrubbing system, the rate of oxidation should be a more complicated function of thiosulfate concentration. Without thiosulfate, oxidation is controlled by absorption of oxygen in the absorber, giving oxidation levels of 15 to 30 % with flue gas from high sulfur coal. At moderate levels of thiosulfate, scrubber oxidation should be completely inhibited, but oxidation in the hold tank and thickener will be limited by the supply of oxygen. The minimum supply of oxygen to the hold tank is the solubility of oxygen in the solution at the scrubber outlet, typically about 0.1 mM at 10 % oxygen in the flue gas. This corresponds to an oxidation level of about 2%. More oxygen will be available if the liquid surface in the hold tank is agitated and exposed to air. At high levels of thiosulfate, oxidation should be controlled by the reaction kinetics represented by Owens' results in Figure 1.

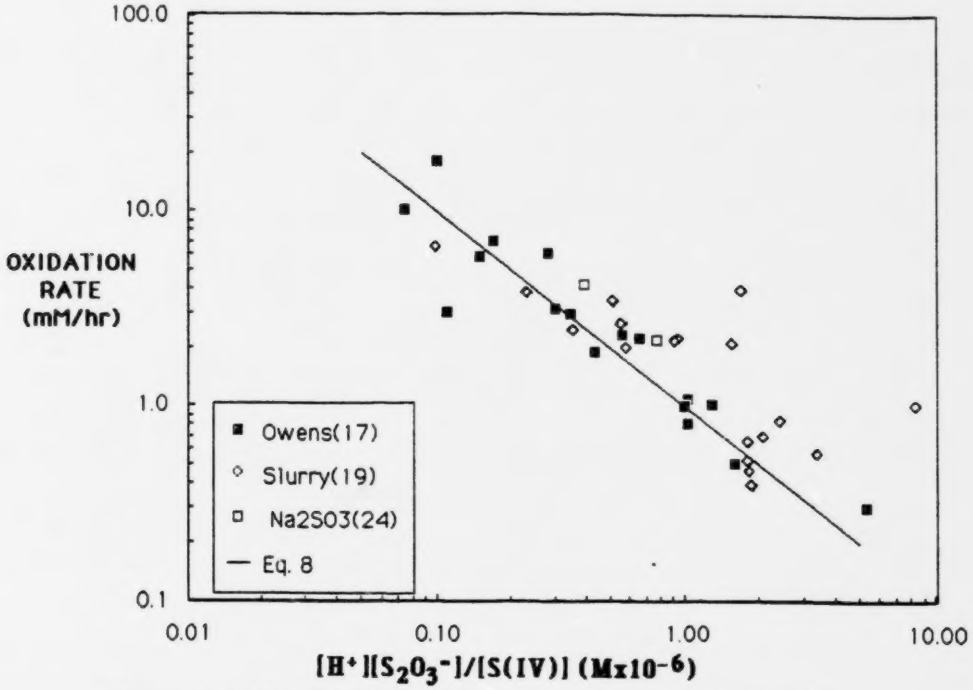


Figure 1. Sulfite oxidation rates at 50°C, inhibited by thiosulfate.

Oxidation rates for the RTP pilot plant have been calculated assuming that all of the oxidation occurs in the hold tank. Without thiosulfate the oxidation rates are typically 10 to 20 mM/hr. With thiosulfate the oxidation rates vary from 0.5 to 4 mM/hr and are correlated by Eq. 8 as shown in Figure 1. The pilot plant data include variation in pH from 5 to 7.5 and in S(IV) from 1.6 to 44 mM. Figure 1 also shows previous results in the pilot plant on oxidation at dual alkali conditions(80 mM S(IV), pH 6.2) (24).

The correlation of Figure 1 represented by Eq. 8 shows that more thiosulfate is required at higher levels of dissolved S(IV) and higher pH. In practice the level of S(IV) is increased in systems with added MgO or Na_2CO_3, along with a reduction in dissolved Ca^{++}. Therefore a higher thiosulfate concentration is required to inhibit oxidation in dual alkali processes or slurry scrubbing processes promoted by MgO. Similarly less thiosulfate is required in slurry scrubbing with high concentrations of $CaCl_2$, because the Ca^{++} reduces the level of dissolved S(IV).

Figure 2 illustrates the correlation of the fraction oxidation in the RTP pilot plant with the inhibitor product. In the pilot plant sulfate is formed not only by S(IV) oxidation but also by hydrolysis of trithionate, the degradation product of thiosulfate. Assuming that trithionate hydrolysis contributes a constant 2% oxidation (corresponding to a hydrolysis rate of 0.6 mM/hr and SO_2 loading of 30 mM/hr), the data are correlated by a modified form of Eq. 9:

$$f_{ox} = 30\times10^{-9}\ M^3/hr\ ([Ca^{++}][S_2O_3^{=}]Ldg)^{-1} + 0.02 \qquad (12)$$

To the extent that calcium concentration can be increased, the effectiveness of thiosulfate as an oxidation inhibitor should be increased.

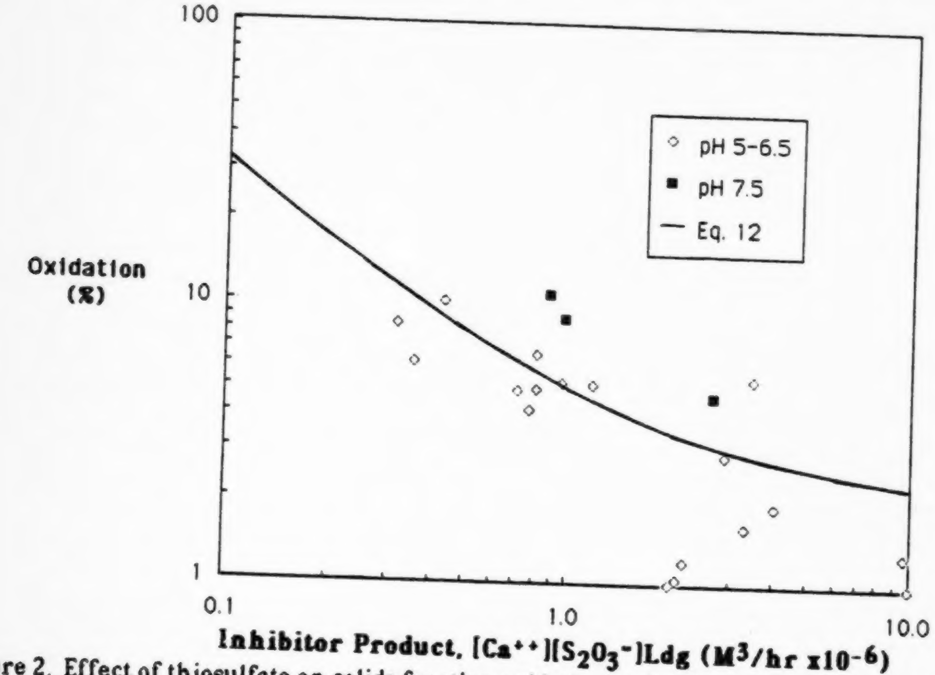


Figure 2. Effect of thiosulfate on solids fraction oxidation at the EPA-RTP pilot plant(19).

GYPSUM SATURATION AND SCALING

When slurry scrubbers operate with sulfite oxidation levels less than 15 or 20% of the SO_2 absorbed, gypsum scaling usually does not occur because the calcium sulfate precipitates as a solid solution with calcium sulfite hemihydrate, rather than as gypsum (calcium sulfate dihydrate). In this case the solution is unsaturated with gypsum. The relative gypsum ($CaSO_4{\cdot}2H_2O$) saturation (RS_{gyp}) was estimated from solution analyses (in moles/liter(M)) by the correlation(25):

$$RS_{gyp} = [Ca^{++}][SO_4^{=}](263/I + 47) \qquad (13)$$

where I = ionic strength = $3[Ca^{++}] + 3[Mg^{++}] + [Na^{+}] + [SO_4^{=}] + [S_2O_3^{=}] + [S_3O_6^{=}]$

The equilibrium of aqueous solution with calcium sulfite solid solution is given in Figure 3 as aqueous solution composition (gypsum saturation) versus solid composition (mole% oxidation). The solid curve, a correlation of laboratory data by Radian(26), is given by the equation:

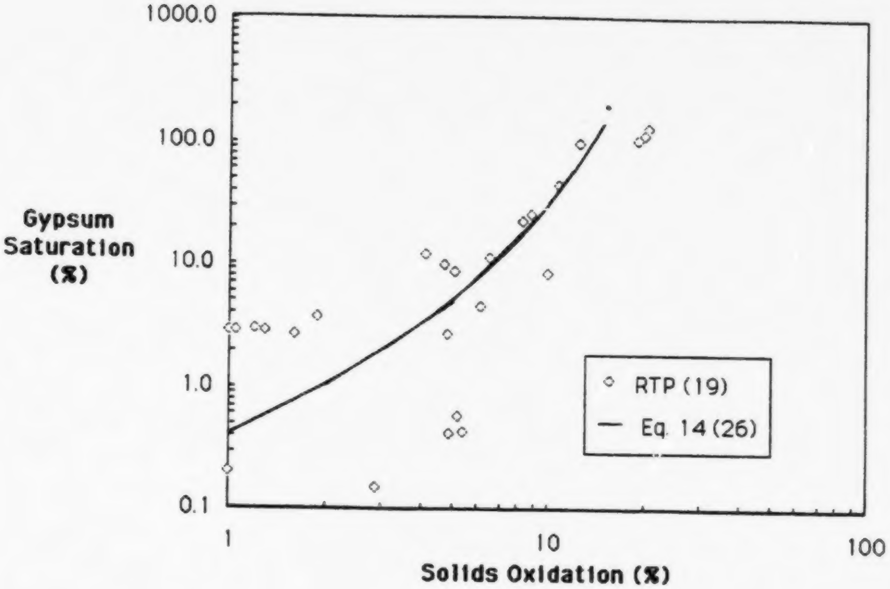


Figure 3. Equilibrium relationship of gypsum saturation with solids oxidation.

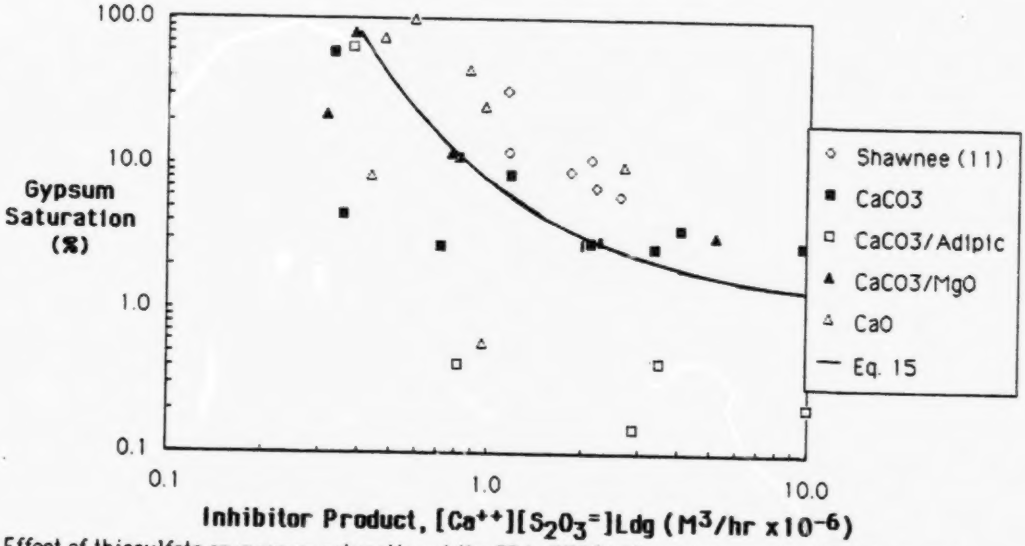


Figure 4. Effect of thiosulfate on gypsum saturation at the EPA-RTP(19) and Shawnee(11) pilot plants.

$$RS_{gyp} = f_{ox} \exp(-1.11 + 22.5 f_{ox}) \qquad (14)$$

As shown in Figure 3, the RTP pilot plant data agree reasonably well with the Radian correlation. The greatest scatter in the data occurs at low oxidation levels where measurement of oxidation and gypsum saturation is very difficult. Sulfate content of the solids and solution plants is calculated by the difference between S(IV) determined by iodometric titration and the sum of sulfate and S(IV) determined by ion chromatography. Data from the Shawnee pilot plant using thiosulfate give an average solids oxidation of 15% with a gypsum saturation of only 13%, well below the Radian correlation, probably because of inaccurate solids analysis.

The effect of thiosulfate on gypsum saturation is shown more directly in Figure 4 which gives the effect of the inhibitor product, $[S_2O_3^{=}][Ca^{++}]Ldg$. Combining Eqs. 12 and 14 gives the relationship shown as the curve on Figure 4:

$$RS_{gyp} = (0.01 + 15.5\text{x}10^{-9}/([Ca^{++}][S_2O_3^{=}]Ldg))\exp(113\text{x}10^{-9}/([Ca^{++}][S_2O_3^{=}]Ldg)) \qquad (15)$$

Figure 4 includes data from RTP and Shawnee. The scatter of the data may result from difficulty in measuring gypsum saturation at low levels. The data from Shawnee generally fall above the RTP correlation. At Seminole Electric, the gypsum saturation varies from 5 to 20% with inhibitor product exceeding $20\text{x}10^{-6}$ M^3/hr. One explanation for higher levels of saturation in the field units could be additional "oxidation" contributed by absorption of SO_3 from the flue gas.

SOLIDS DEWATERING

The dewatering properties of calcium sulfite solids are improved by reducing their sulfate content. The crystallization of calcium sulfite is inhibited by increased gypsum saturation (dissolved calcium sulfate). Tseng (27,28) found that the growth rate of one crystal face is inhibited by sulfate and that the thickness of individual platelets increases as solid sulfate content decreases: 10% oxidation gave 0.01 µm platelets, 3% oxidation gave 0.1 µm platelets, and 1% oxidation gave 2 µm platelets. Chang et al.(24) found that dewatering properties of dual alkali solids were improved by operating at conditions giving lower levels of solids oxidation.

Improved dewatering has not been observed in any of the commercial plants using lime scrubbing. The initial work with limestone at Shawnee suggested that the filter cake solids content increased from 40 to 80 % when operating with an excessive level of thiosulfate (29). However this observation was not included in the written report (10) because of uncertainties and unsteady state behavior associated with frequent changes in the dewatering configuration. Later work at Shawnee (11) using 2 mM thiosulfate showed a definite increase from 65 to 85% solids in the filter cake and from 0.35 to 0.65 cm/min initial settling rate when an inhibitor product greater than 10^{-6} M^3/hr was used. These tests with 15% limestone scrubbing slurry included about 40% flyash in the waste solids.

In the pilot plant work at RTP, thiosulfate addition enhanced filter cake solids from 56% to as high as 78% (Figure 5) and initial settling rate from 0.7 to as high as 3.6 cm/min (Figure 6). Dewatering enhancement was observed at RTP whenever the measured solids oxidation was less than 2%. Table 2 shows that mass mean particle diameter measured by a Coulter counter increased at higher inhibitor product with a resulting enhancement of dewatering properties. Run LS-5 was at a much higher inhibitor product because of the addition of calcium chloride. Figures 7 to 9 are pictures of solids from the three runs in Table 2 taken with a scanning electron microscope. As solids oxidation is inhibited, the solids appear to change from thin platelets to bulky crystals.

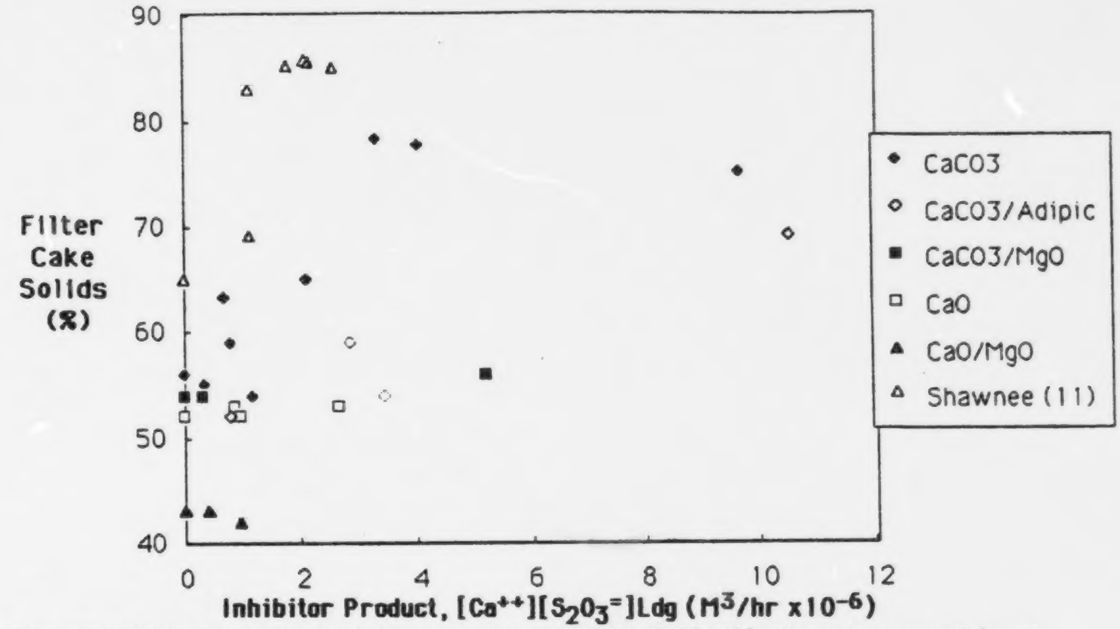


Figure 5. Effect of thiosulfate on filter cake solids at the EPA-RTP(19)(with various reagents) and Shawnee(11)(limestone) pilot plants.

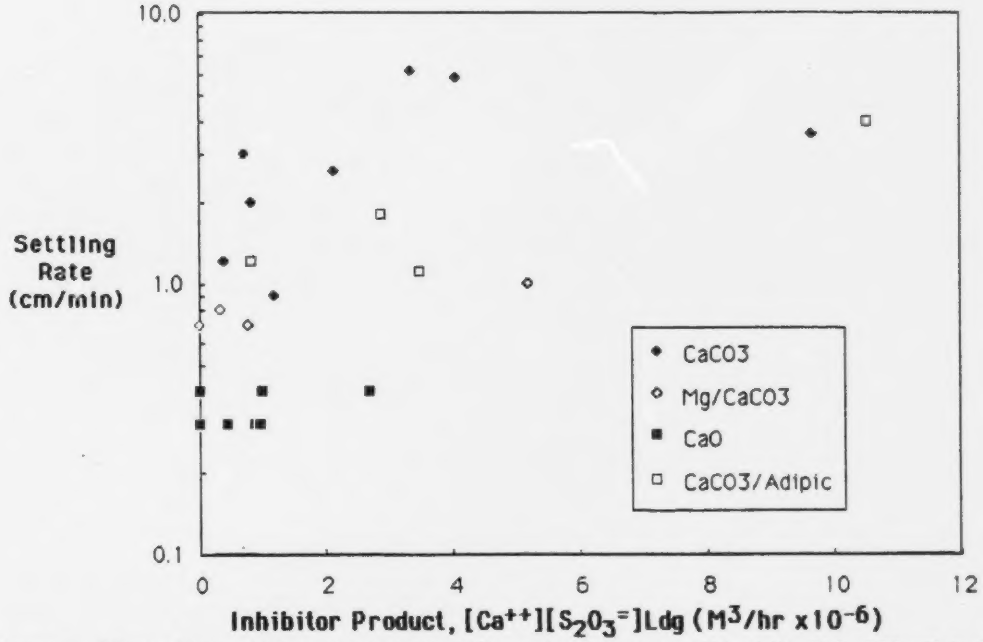


Figure 6. Effect of thiosulfate on the initial settling rate of product solids at the EPA-RTP pilot plant with various reagents.

Table 2. DEWATERING WITH LIMESTONE AT THE EPA-RTP PILOT PLANT(19)

Run No.	LS-0	LS-4	LS-5
$S_2O_3^=$ (mM)	0	20.1	8.9
Cl^- (mM)	1.7	1.9	86
Ca^{++}(mM)	22	3.6	35
Oxidation (%)	20.6	1.2	1.3
Settling Rate (cm/min)	0.7	2.6	3.6
Filter Cake Solids (%)	56	65	75
Mass median particle diameter (μm)	12	14	28
Diameter range including 90 wt% of the sample (μm)	6-21	7-24	10-50

With limestone alone, dewatering was enhanced at an inhibitor product greater than $3x10^{-6}$ M^3/hr, usually achieved with addition of both thiosulfate and calcium chloride. The RTP tests were made without flyash, which may have enhanced the dewatering effect at Shawnee.

Using limestone with 15 mM adipic acid, dewatering enhancement was not observed at an inhibitor product of $3.5x10^{-6}$ M^3/hr but was observed at $10.5x10^{-6}$ M^3/hr. It is known that adipic acid coprecipitates with calcium sulfite in the same way that sulfate does(30,31), and it may also inhibit crystal growth.

No dewatering enhancement was observed with limestone scrubbing using Mg promotion or with lime scrubbing; however, the inhibitor product did not exceed $5x10^{-6}$ M^3/hr in any of these series. In these lime/limestone systems high concentrations of thiosulfate are needed to get high inhibition levels; therefore, it is improbable that enhanced dewatering will be an important effect. In lime scrubbing, reduced oxidation levels may not enhance dewatering because the calcium sulfite solids typically crystallize as agglomerates rather than single platelets. The tests involving Mg may have had artificially high oxidation levels because of the addition of magnesium sulfate to maintain the Mg concentration in the pilot plant. In commercial systems Mg would be added as MgO or $MgCO_3$ and would not contribute sulfate.

Mg has been reported to degrade dewatering properties of calcium sulfite solids from limestone dual alkali systems at Mg/Ca ratios as low as 30 mole/mole in the solution (32). The RTP limestone runs promoted by Mg and by adipic acid had Mg/Ca ratios as large as 12-15 at high thiosulfate concentration where dewatering was not enhanced.

At Seminole Electric, the filter cake improved from 50 to 80% solids with the addition of thiosulfate to give an inhibitor product exceeding $20x10^{-6}$ M^3/hr in the high chloride limestone scrubber(20).

SO_2 REMOVAL AND LIMESTONE UTILIZATION

In systems where charge balance dictates a ratio of dissolved sulfate to calcium greater than 1 (with $2[Mg^{++}] + [Na^+] > [Cl^-]$), a reduction in gypsum saturation (caused by thiosulfate addition or otherwise) will result in a significant decrease of dissolved calcium. As a result SO_2 removal and/or limestone dissolution will occur more readily. In the tests at Shawnee(11), dissolved calcium decreased from 22 to 3 mM with the addition of 6 mM thiosulfate. In tests

Reproduced from best available copy.

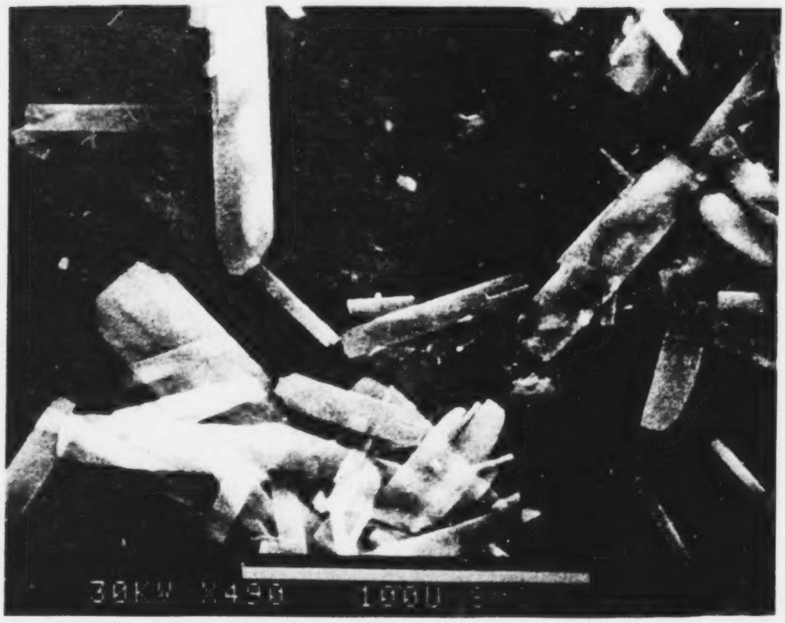

30KV X490 100U

Figure 7. Solid product from EPA-RTP using limestone without thiosulfate (500x).

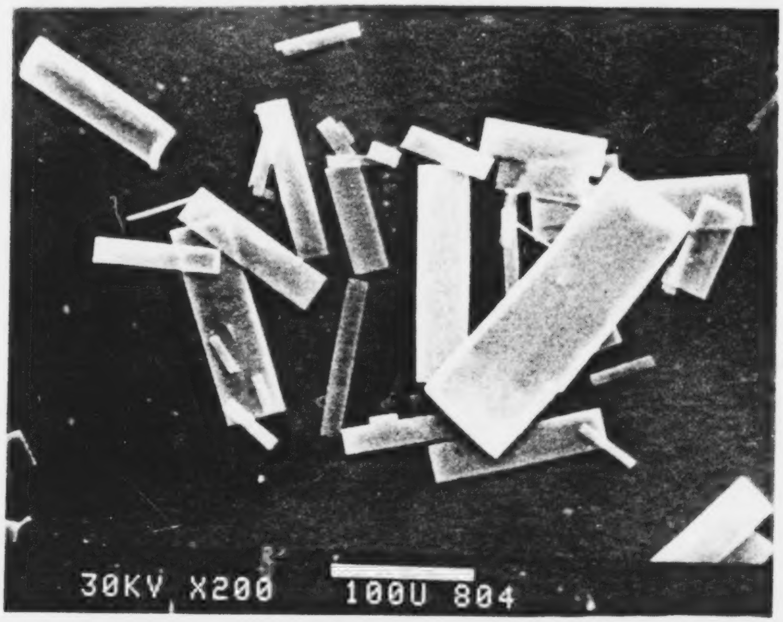

30KV X200 100U 804

Figure 8. Solid product from EPA-RTP using limestone with 20 mM thiosulfate (200x).

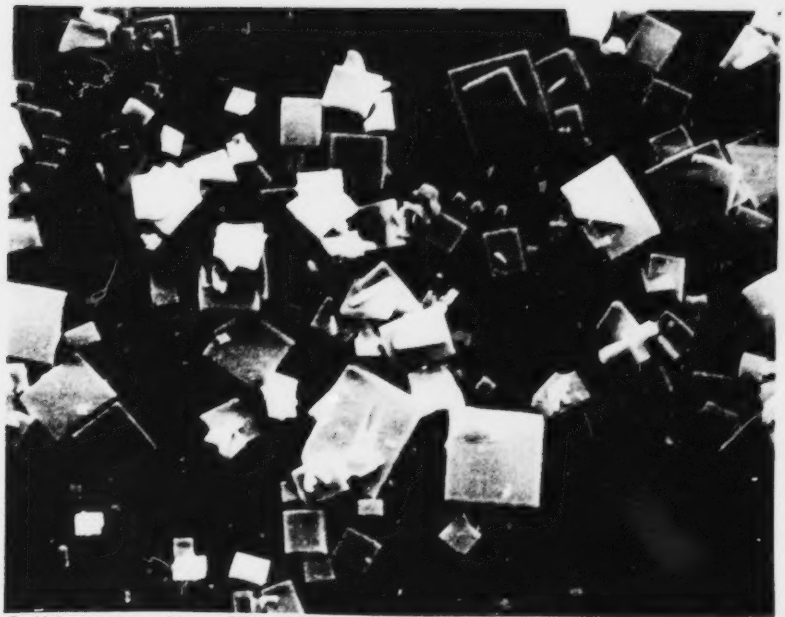


Figure 9. Solid product from EPA-RTP using limestone with 86 mM Cl^- and 9 mM $S_2O_3^=$.

without added chloride at RTP, the dissolved calcium decreased from 25 to 6 mM with limestone, from 18 to 3.5 mM with Mg-promoted limestone, and from 16 to 1 mM with Mg-promoted lime.

Reduced calcium [redacted]es SO_2 removal by increasing dissolved sulfite alkalinity through the equilibrium reaction:

$$CaSO_3(s) \longleftrightarrow Ca^{++} + SO_3^= \tag{16}$$

$$[SO_3^=] = K_{sp}/[Ca^{++}] \tag{17}$$

Dissolved sulfite reduces the liquid film resistance to mass transfer in the scrubber. This effect should be especially pronounced in Mg-promoted systems where dissolved sulfite is already high. However, the maximum enhancement of SO_2 removal is limited by gas film resistance. No effect of thiosulfate on SO_2 removal was observed at Shawnee or at RTP without Mg promotion. However at RTP with limestone promoted by 50 mM Mg, the SO_2 removal increased from 83 to 88% with the addition of 8 mM thiosulfate. In lime scrubbing promoted by 84 mM Mg, the SO_2 removal increased from 95 to 98% with the addition of 27 mM thiosulfate. At the Phillips Station of Duquesne Light, the presence of about 3 mM thiosulfate in a lime scrubber promoted by MgO enhanced SO_2 removal from 83 to 88% (7).

Reduced dissolved calcium should also enhance limestone dissolution and increase equilibrium pH in the hold tank through the reaction:

$$CaCO_3(s) + 2H^+ \longrightarrow Ca^{++} + CO_2 + H_2O \tag{18}$$

$$[H^+]^2 = K[Ca^{++}]P_{CO2} \tag{19}$$

In the Shawnee tests(11), the hold tank pH was controlled at 5.8 as thiosulfate concentration was increased to 6 mM and the limestone utilization increased from 75 to 90%. In the RTP work, the pH was controlled at 5.5 as thiosulfate was added. With limestone alone or with 14 mM adipic acid, the limestone utilization increased from 86 to 97% with the addition of 20 mM thiosulfate. With 51 mM Mg, the limestone utilization increased from 88 to 94% with the addition of 62 mM thiosulfate. Because Mg^{++} inhibits limestone dissolution(32,33), the effect of thiosulfate on limestone utilization will not be as great in Mg-promoted systems. If limestone utilization is held constant as thiosulfate is added to the system, the hold tank pH should increase and SO_2 removal should be enhanced by increased dissolved bicarbonate.

The use of thiosulfate tends to increase the accumulated concentration of Mg by increasing dissolution of $MgCO_3$ in the limestone and by enhancing dewatering of waste solids. At Shawnee the Mg concentration increased from 28 to 40 mM with an inhibitor product of $2x10^{-6}$ M^3/hr (11). At RTP the Mg concentration increased from 13 to 40 mM with an inhibitor product of 10^{-6} M^3/hr(19).

ORGANIC ACID MAKEUP RATE

The makeup rate for organic acid additive, such as adipic acid or dibasic waste acid (DBA), may be reduced by the addition of thiosulfate. Improved dewatering of waste solids should reduce solution losses of additive. Oxidative degradation of organic acids is proportional to sulfite oxidation and should be reduced to the extent that thiosulfate inhibits oxidation (8). Loss of organic acid by coprecipitation with calcium sulfite is inversely proportional to dissolved calcium(30). However, coprecipitation losses increase as solids oxidation decreases(31).

A series of runs was performed at RTP with a constant rate of adipic acid addition (4.2 mmole/mole SO_2 absorbed) to a limestone scrubber. The steady state adipic acid concentration was about 14 mM for a range of thiosulfate from 0 to 20 mM with very little change in the filter cake solids concentration. Losses of adipic acid by degradation and coprecipitation were about 1.8 mmole/mole SO_2 absorbed. This result suggests that the expected reduction in degradation was balanced by an increase in coprecipitation. Assuming that none of the unexplained losses are due to degradation when using greater than 5 mM thiosulfate, the extent of coprecipitation corresponds to 1.0 ppm adipic acid in solids per ppm adipic acid in solution. This value is close to that predicted from previous data on coprecipitation(30,31). Higher levels of thiosulfate in combination with adipic acid should reduce adipic acid makeup by reducing solution content in the waste solids.

THIOSULFATE DEGRADATION AND MAKEUP

Makeup of thiosulfate is necessary to replace losses of thiosulfate and trithionate in solution entrained with waste solids. As thiosulfate inhibits oxidation, it is oxidized to tetrathionate. Tetrathionate reacts quickly with sulfite to make trithionate and regenerate some thiosulfate. Trithionate hydrolyzes slowly to make sulfate and regenerate the rest of the thiosulfate. The trithionate accumulates to a steady-state concentration of 5 to 20 mM. Actual makeup costs vary from $0.20 to 3.00/tonne limestone and $3 to 14/tonne lime.

THIOSULFATE OXIDATION

Most oxidizing environments, including iodine(I_2), cupric(Cu^{++}), hydrogen peroxide(H_2O_2), and electrochemical anodes, convert thiosulfate initially to tetrathionate ($S_4O_6^{=}$)(23). Thiosulfate oxidation probably occurs by reaction of thiosulfate with a free radical to form a thiosulfate radical (Rxn. 3), followed by second order reaction of thiosulfate radicals to give tetrathionate (Rxn. 4). The measured rate of Rxn. 4 (3.5×10^9 $M^{-1}sec^{-1}$(34), 8×10^8 $M^{-1}sec^{-1}$(35)) is comparable to the rates of other radical terminating reactions involving sulfite radical ($SO_3^{-\cdot}$) or peroxymonosulfate radical ($SO_5^{-\cdot}$) (36).

In the presence of sulfite, tetrathionate is rapidly converted to trithionate by the reversible reaction:

$$S_4O_6^{=} + SO_3^{=} \longleftrightarrow S_3O_6^{=} + S_2O_3^{=} \qquad (20)$$

The forward rate of this reaction has been measured by Owens (18) at 50°C and pH 4.5 to 5.5 in 0.3 M Na_2SO_4 with 0.01 M S(IV) and 0.0125 M $Na_2S_4O_6$. The activation energy was estimated to be 13.4 kcal/gmol using Davis (37, Eq. 4c). The effect of ionic strength attributed to cations (I_+) was taken from Rochelle (38, Fig. 3-4). Owens' data are correlated by:

$$r_f = k_f[S_4O_6^{=}][SO_3^{=}] \text{ (M/s)} \qquad (21)$$

$$k_f = 7.3 \times 10^9 \exp(5I_+^{0.5}/(1 + I_+^{0.5}) - 6744/T) \qquad (22)$$

Earlier measurements at lower ionic strength (8-16 mM), 0°C, and pH 9 gave a proportionality constant of 9×10^9 $M^{-1}s^{-1}$(39) compared to 7.3×10^9. Measurements at pH 1.7, 10 to 40°C, and $I_+ = 2$ M, gave much lower rates and suggest that bisulfite does not react with tetrathionate as fast as sulfite (40). Similarly the reverse rate of Rxn. 20 is given by(41-43):

$$r_r = k_r[S_3O_6^{=}][S_2O_3^{=}] \text{ (M/s)}$$

$$k_r = 2.2 \times 10^4 \exp(5I_+^{0.5}/(1 + I_+^{0.5}) - 6417/T) \qquad (23)$$

The equilibrium for Rxn. 20 can be determined by setting the reverse rate equal to the forward rate :

$$K = ([S_3O_6^{=}][S_2O_3^{=}])/([S_4O_6^{=}][SO_3^{=}]) = 3.3 \times 10^5 \exp(-327/T) \qquad (24)$$

At 50°C the equilibrium constant is 1.2×10^5. With 1 mM sulfite, 10 mM thiosulfate, and 10 mM trithionate, the equilibrium tetrathionate concentration is only 10^{-5} mM and the pseudo-first-order forward rate constant is 0.4 min^{-1}. Therefore, at most conditions tetrathionate is converted very quickly to trithionate. At very low sulfite (at low pH or at points where all of the sulfite is lost to oxidation), it may be possible to get a significant concentration of tetrathionate.

Owens(18) measured the net rate of oxidation of thiosulfate to trithionate at 50°C in 0.3 M Na_2SO_4 with 3 to 30 mM S(IV):

$$S_2O_3^{=} + SO_3^{=} + 0.5O_2 + H_2O \longrightarrow S_3O_6^{=} + 2OH^- \qquad (25)$$

Assuming that thiosulfate terminates all of the free radicals formed in sulfite oxidation, the rate of Rxn. 20, r_{deg}, is equal to half the rate of free radical initiation, r_i. At higher thiosulfate concentrations ($[S_2O_3^{=}]/[S(IV)] > 0.1$), Owens found that the thiosulfate degradation rate, r_{deg}, was independent of thiosulfate concentration. His results were not always reproducible, but suggest degradation rates from 0.4 to 1 mM/hr at pH 5 with greater than 0.001 mM Fe. The degradation rates appeared to be somewhat higher at pH 6 (0.4 to 2 mM/hr) and somewhat lower at pH 4.5 (0.2 to 0.7 mM/hr).

At lower concentrations of thiosulfate ($[S_2O_3^{=}]/[S(IV)] < 0.1$), Owens found that the thiosulfate degradation rate increased as thiosulfate concentration decreased. At pH 5 the rate of degradation was correlated with the rate of sulfite oxidation by:

$$r_{deg}\,(M/hr) = 6.2([Fe]r_{ox})^{0.5} \quad (M/hr) \qquad (26)$$

HYDROLYSIS OF TRITHIONATE

At pH 2 to 12 trithionate reacts slowly with water to regenerate thiosulfate(43-51):

$$S_3O_6^= + H_2O \longrightarrow S_2O_3^= + SO_4^= + 2H^+ \qquad (27)$$

$$r_h = k_h[S_3O_6^=] \qquad (28)$$

Figure 10 gives the first order rate constant for this reaction as a function of temperature. The best data are probably those of Naito et al. (43) which give a rate of 0.035 hr^{-1} at 55°C. Naito's data are correlated by the equation:

$$k_h = 1.5x10^{12}\,exp(-10{,}166/T)\ (hr^{-1}) \qquad (29)$$

The net effect of thiosulfate oxidation (Rxn. 25) and hydrolysis (Rxn. 27) is oxidation of S(IV) to sulfate, with no loss of thiosulfate. In a scrubber system where thiosulfate oxidation and hydrolysis both occur in the same well-mixed solution volume, for example the hold tank, the trithionate concentration should reach a steady-state concentration given by:

$$[S_3O_6^=] = r_{deg}t/(1 + k_ht) \qquad (30)$$

The system residence time, t, is defined as the ratio of system solution volume (hold tank + thickener) to the rate of solution loss from the system (filter cake + other losses). With large residence time (>100 hr), typical of syste[illegible]ith good dewatering, the steady-state trithionate

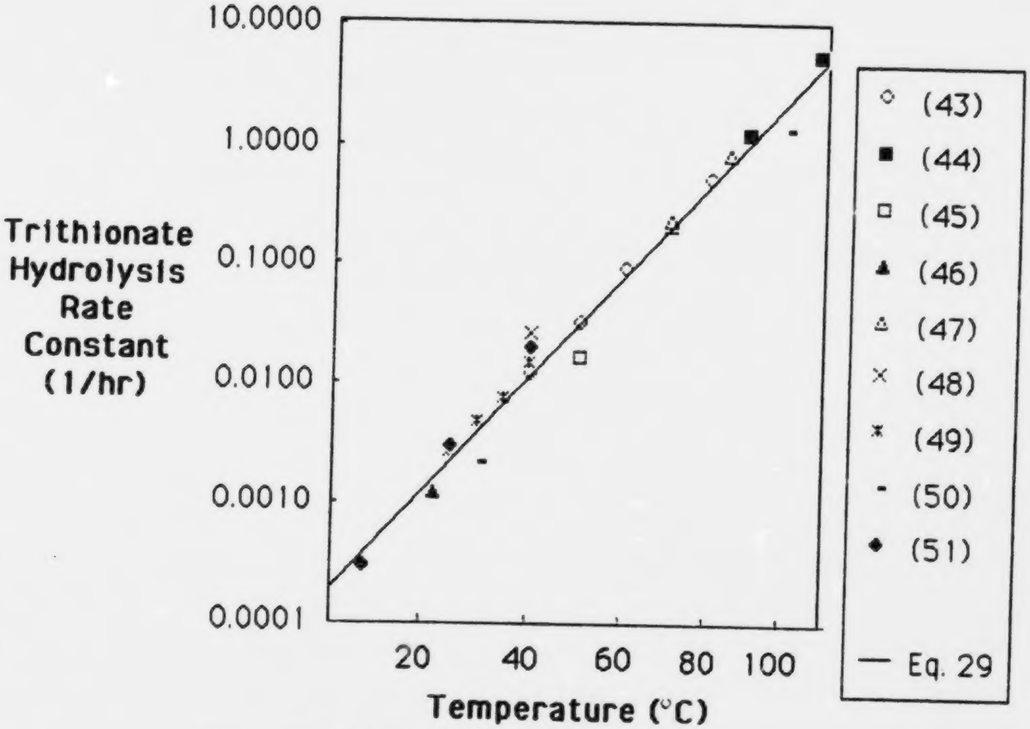


Figure 10. Trithionate hydrolysis rate at pH 2 to 12.

concentration is independent of residence time and is given by:

$$[S_3O_6^{=}] = r_{deg}/k_h \quad (31)$$

At 55°C with r_{deg}=0.5 mM/hr, the trithionate concentration should be 14 mM. To the extent that oxygen is unavailable at locations such as the thickener, hydrolysis will occur but thiosulfate oxidation will not. Therefore steady-state trithionate concentration will be proportionately smaller.

Battelle has analyzed solutions from three of the Shawnee runs with thiosulfate by modified ion chromatographic methods for dithionate and polythionates(14). These analyses were made several months after the samples were collected and may not be representative. They found 3 to 4 mM trithionate and 0.5 to 1 mM dithionate in most of the samples. Only one sample of thickener overflow had a significant concentration of other polythionates (1.3 mM tetrathionate).

With data from Shawnee and RTP, the steady-state concentration of trithionate and other degradation products can be estimated by difference from total sulfur analyses and by difference from sodium analyses assuming a constant background level of sodium. At Shawnee the concentration of degradation products (expressed as trithionate) was 6 to 10 mM from total sulfur and about 10 mM based on sodium analysis. Thickener underflow consistently contained 1.5 to 3 mM more thiosulfate and less trithionate than scrubber solution, suggesting that hydrolysis was occurring in the thickener, without corresponding thiosulfate oxidation. The earliest run at Shawnee suggested trithionate of 15 mM from total sulfur and 21 mM from sodium(10).

At RTP total sulfur analyses were not consistent and suggest trithionate concentrations from 0 to 20 mM. Sodium balances suggest 5 to 10 mM trithionate with as much as 18 mM in the runs with lime alone. The trithionate level was not a function of thiosulfate concentration at either Shawnee or RTP. Based on the overall sodium balance, the system solution residence time, t, was in the range of 110 to 660 hours. Therefore, Eq. 26 can be used to estimate r_{deg}. Assuming that degradation occurs only in the hold tank and that hydrolysis occurs throughout the system, r_{deg} is estimated to be 0.6 mM/hr for 10 mM trithionate. A comparable estimate for the recent Shawnee data gives r_{deg} = 1.6 mM because of the relatively larger thickener.

MAKEUP REQUIREMENTS

Thiosulfate must be added to the sustem at a rate equal to solution losses of thiosulfate and equivalent trithionate. Because trithionate is usually present at a constant level, makeup rates are a weaker function of thiosulfate than might be expected. Heavy initial doses of thiosulfate have also been required at both RTP and Shawnee to provide the minimum inventory of trithionate before a significant concentration of thiosulfate could be maintained. Because thiosulfate actually degrades somewhat faster at lower concentrations and because a small change of thiosulfate makeup rate can make a large change in thiosulfate concentration, neither Shawnee nor RTP was able to maintain constant thiosulfate concentration at less than about 3 mM.

In the RTP tests, the minimum makeup rate needed to maintain some thiosulfate concentration was 1.3 mmole thiosulfate/mole SO_2 absorbed and makeup rates as high as 10.7 mmole/mole SO_2 were used to obtain 27 mM thiosulfate. However, solution losses are abnormally high at RTP. Estimates of solution losses for these two cases based on filter cake solids concentration give makeup rates of 0.7 and 2.0 mmole/mole SO_2, respectively. Makeup rates at Shawnee varied from 0.4 to 1.2 mmoles/mole SO_2. Makeup rates in the Duquesne Light scrubbers using lime promoted by MgO have been about 3.5 mmole/mole SO_2 (7). In the high chloride limestone scrubbers at Seminole Electric, thiosulfate makeup appears to be about 1.5 mmole/mole SO_2 based on preliminary results(20).

Table 3 gives thiosulfate makeup rates estimated for several potential applications. At $120/kg-mole thiosulfate, the makeup rate is about equal to the cost in dollars for thiosulfate makeup per tonne $CaCO_3$. Two different levels of thiosulfate have been included, one to get 10% gypsum saturation and one to get significant enhancement of solids dewatering. Thiosulfate is most attractive in limestone systems with some chlorides, where little additional thiosulfate concentration is required to enhance dewatering and thereby greatly reduce net makeup. Without chloride, enhanced dewatering can require very large increases in thiosulfate concentration which negate any reduction in solution loss.

Table 3. ESTIMATED THIOSULFATE MAKEUP FOR TYPICAL APPLICATIONS
Basis: 50% solids without thiosulfate, 50 mM/hr SO_2 loading in hold tank

	Solution Composition (mM)			Gypsum	Filter Cake	Makeup
Case	Ca^{++}	$S_2O_3^=$	$S_3O_6^=$	Sat. (%)	(% solids)	(mmole/mole SO_2)
$CaCO_3$	6	3.5	12	10	55	1.6
	2	30	10	1	80	1.3
+Chloride	100	0.6	10	1	80	0.3
+MgO	4	15	12	10	55	1.7
	1	60	10	1	80	2.0
CaO (pH 7.5)	5	20	20	10	50	5.2
+Chloride	100	1	20	10	50	2.7
+MgO (pH 6.5)	5	12	15	10	50	3.5

SOURCES OF THIOSULFATE

Sodium thiosulfate is available from Ferro Corporation/Grant Chemical as 30 wt% solution at $73/kg-mole (FOB Baton Rouge, LA) or from Allied Chemical as anhydrous or pentahydrate solid at $157/kg-mole (FOB Claymont, DE). The current production capacity is on the order of 30,000 tonne/yr with actual production closer to 15,000 tonne/yr(52). Duquesne Light has used bags of anhydrous thiosulfate. Seminole Electric is using the solution.

Ammonium thiosulfate is an alternative direct source of thiosulfate that is produced in greater quantity (100,000 tonne/yr) at lower cost ($70/kg-mole)(52). It is distributed as 60 wt% solution. It would probably not be suitable for use in lime systems because ammonia volatility could be a problem at the high pH. Ammonia might also be an objectionable nutrient in any waste water.

Thiosulfate can also be produced in situ by reaction of sodium sulfide (Na_2S) or sodium polysulfide (Na_2S_n) with sulfite(52,53). Sodium sulfide is available as 45 wt% solution at an equivalent cost of $21/kg-mole thiosulfate, assuming that 2 moles of thiosulfate can be obtained from 1 mole of sulfide. Sodium polysulfide can be prepared by dissolving elemental sulfur (powdered) in concentrated sodium hydroxide(52) or sodium sulfide solution(54). Sodium tetrasulfide (Na_2S_4) is available as 34 wt% solution at an equivalent cost of $17/kg-mole thiosulfate, assuming that 3 moles of thiosulfate are obtained from 1 mole of sodium tetrasulfide(55).

The Stretford process for removal of hydrogen sulfide from fuel gases produces a waste solution typically containing 10 to 25 wt% sodium thiosulfate with 4% sodium sulfate, 5% sodium carbonate, 0.4% vanadium, and 0.2% anthraquinone disulfonate. From 1 to 5 mole % of the sulfur absorbed by the Stretford process is converted to thiosulfate. There are 13 Stretford plants in the U. S. with the capacities greater that 15 tonne/day, amounting to a total potential thiosulfate source of 2,000 to 10,000 tonne of sodium thiosulfate per year(56). This could be an inexpensive source of thiosulfate if the impurities can be tolerated.

CONCLUSIONS

1. Sodium thiosulfate is an effective additive for inhibiting sulfite oxidation. The inhibiting effectiveness is proportional to the ratio of thiosulfate and sulfite and in slurry scrubbing processes is approximately proportional to the product of thiosulfate, dissolved calcium, and SO_2 loading in the hold tank (defined as the inhibitor product). Therefore thiosulfate is most effective in limestone scrubbers with high chloride and least effective in MgO-promoted lime scrubbers.

2. Gypsum saturation was significantly reduced and scaling was eliminated in all slurry scrubbing processes tested with an inhibitor product as low as 0.3×10^{-6} M^3/hr.

3. Solids dewatering is enhanced at high levels of thiosulfate in limestone scrubbers with and without organic acids. In Shawnee tests filter cake solid increased from 65 to 85% and settling rates increased 0.35 to 0.65 cm/min with an inhibitor product of 10^{-6} M^3/hr. At RTP filter cake solids increased from 55 to 75% and settling rates increased from 0.6 to 3 cm/min at an inhibitor product of 4×10^{-6} M^3/hr.

4. SO_2 removal and limestone utilization are increased by addition of thiosulfate to scrubbers with low or moderate levels of dissolved calcium. Increased SO_2 removal has been demonstrated in lime and limestone scrubbers promoted by MgO. Increased limestone utilization has been demonstrated in limestone scrubbers with low chloride.

5. The net consumption of adipic acid in a limestone scrubber was not reduced by addition of thiosulfate. Reduced degradation of adipic acid was probably offset by increased coprecipitation with calcium sulfite.

6. As thiosulfate inhibits oxidation by scavenging free radicals, it is converted to trithionate. Trithionate hydrolyzes to regenerate thiosulfate, but must accumulate to a steady-state level before thiosulfate will accumulate. Therefore, the minimum addition rate of thiosulfate must provide an effective thiosulfate concentration of 10 to 20 mM. Furthermore, the scrubber must be spiked to this level before any thiosulfate concentration can be maintained.

7. Practical thiosulfate makeup rates vary from 0.3 mmole/mole SO_2 removed for limestone scrubbing with chloride to 5.2 for lime scrubbing at pH 7.5. Using sodium thiosulfate, these rates correspond to a cost range of $0.20 to 3.00/tonne limestone and $3 to 14/tonne lime.

8. Sodium thiosulfate is a practical, demonstrated additive available as concentrated solution at $73/kg-mole or as solid at $157/kg-mole. Ammonium thiosulfate, sodium polysulfide, and waste solution from Stretford processes could be used at costs as low as $17/kg-mole thiosulfate, but have not been tested.

REFERENCES

1. Potts, J. M., J. E. Jordan, et al. Removal of Sulfur Oxides from Waste Gases. Monthly Progress Report, Applied Research Branch, Division of Fertilizer Development, Tennessee Valley Authority, October 1972.

2. Gogineni, M. R., J. R. Martin, and P. G. Maurin. Status of C-E's Air Quality Control Systems. In: Proceedings: Flue Gas Desulfurization Symposium--1973, EPA-650/2-73-038 (NTIS No. PB230-901), pp. 539-552, December 1973.

3. Inoue, J., K. Ueda, and T. Komatsu. Antioxidation of Sulfite Aqueous Solutions. Japan. Kokai 75,125,993, 1974 (Chem. Abstr. 84:107943).

4. Holcombe, L. J. and K. W. Luke. Characterization of Carbide Lime to Identify Sulfite Oxidation Inhibitors. EPA-600/7-78-176 (NTIS No. PB286-646), September 1978.

5. Borgwardt, R. H. Limestone Scrubbing of SO_2 at EPA/RTP Pilot Plant. Progress Report No. 36. October 1978.

6. Hudson, J. L. Sulfur Dioxide Oxidation in Scrubber Systems. Monthly Progress Report, EPA Grant R805227-02, March 1979.

7. Miller, J. F. et al. Lime/Limestone Scrubber Modifications: Investigation of Thiosulfate as an Oxidation/Scaling Inhibitor. DOE/TIC-2005972, December 1981.

8. Rochelle, G. T. et al. Buffer Additives for Lime/Limestone Slurry Scrubbing. ACS Symp. Ser. 188:243-266, 1982.

9. Prada, R. E. Oxygen Absorption Enhanced by Sulfite Oxidation Catalyzed with Manganese and Iron. M. S. Thesis, The University of Texas at Austin, 1981.

10. Wang, S-C. et al. Testing of Sodium Thiosulfate as Oxidation Inhibitor in a Limestone FGD Scrubber at the DOE Shawnee Test Facility. Final Report DOE Contract No. DE-AC21-81MC16427, October 1981. (Also in Ref. 7.)

11. Barkley, J. B. et al. Evaluation of Sodium Thiosulfate Additive on the Performance of a Spray Tower Scrubber System Using Limestone Slurry. TVA/OP/EDT-84/7, November 1983.

12. Barkley, J. B. et al. Sodium Thiosulfate Additive as an Oxidation Inhibitor in a Limestone Spray Tower Scrubber Process. Presented at the APCA Annual Meeting, Atlanta, June 19-24, 1983.

13. Garrison, F. C. and W. L. Wells. Dewatering of Flue Gas Desulfurization Sulfite Solids. U. S. Patent 4,454,101, June 12, 1984.

14. Miller, J.F. et al. Thiosulfate in Limestone Flue Gas Desulfurization Scrubbing. Final report of TVA Contract TV 36914 A, November 1982.

15. Ulrich, R. K. and G. T. Rochelle. Buffer Additives for Lime/Limestone Slurry Scrubbing: Sulfite Oxidation with Enhanced Oxygen Absorption Catalyzed by Transition Metals. EPA-600/7-84-058 (NTIS No. PB84-189950), April 1984.

16. Ulrich, R. K., G. T. Rochelle, and R. E. Prada. Enhanced Oxygen Absorption into Bisulfite Solutions Containing Metal Ion Catalysts. Submitted to Chem. Eng. Sci., March 1985.

17. Owens, D. R. and G. T. Rochelle. Sulfite Oxidation Inhibited by Thiosulfate. M. S. Thesis, University of Texas at Austin. 1984. (Also EPA Draft Report on Purchase Order No. 3D3744NAEX, 1985)

18. Owens, D. R. and G. T. Rochelle, Sulfite Oxidation Inhibited by Thiosulfate. To be Presented at the International Conference on Processing and Utilization of High Sulfur Coals, Columbus, OH, October 13-17, 1985.

19. Chang, J. C. S. and T. G. Brna. Pilot Testing of Sodium Thiosulfate for Oxidation/Scaling Inhibition in Lime/Limestone Flue Gas Desulfurization Systems. To be presented at the AIChE Annual Meeting, Chicago, IL, November 1985.

20. Laslo, D. and E. Bakke. State-of-the-Art Design Application on a Closed Loop FGD System. Presented at the Ninth Symposium on Flue Gas Desulfurization, Cincinnati, OH, June 4-7, 1985.

21. Sillen, L. G. and A. E. Martell. Stability Constants of Metal Ion Complexes. The Chemical Society, 1964.

22. Hayon, E., A. Treinin, and J. Wilf. Electronic Spectra, Photochemistry and Autoxidation Mechanism of the Sulfite-Bisulfite-Pyrosulfite Systems. J. Am. Chem. Soc. 94: 47 (1972).

23. Goehring,M. Die Chemie der Polythionsauren. Fortschr. Chem. Forsch. 2:444-483, 1952.

24. Chang, J. C. S. and N. Kaplan. Pilot Evaluation of Limestone Regenerated Dual Alkali Process. In: Proceedings: Eighth Symposium on Flue Gas Desulfurization, New Orleans, LA, November 1983, V. 1. EPA-600/9-84-017a (NTIS No. PB84-223031), pp. 300-321, July 1984.

25. Head, H. N. EPA Alkali Scrubbing Test Facility: Advanced Program, Third Progress Report. EPA-600/7-77-105 (NTIS No. PB274-544), September 1977.

26. Jones, B. F., P. S. Lowell, and F. B. Meserole. Experimental and Theoretical Studies of Solid Solution Formation in Lime and Limestone SO_2 Scrubbers, V. I. EPA-600/2-76-273a (NTIS No. PB264-953), October 1976.

27. Tseng, P. Calcium Sulfite Hemihydrate Dissolution and Crystallization. Ph.D. Dissertation, The University of Texas At Austin, August 1984.

28. Tseng, P. and G.T. Rochelle. Crystallization of Calcium Sulfite Hemihydrate. Env. Prog. in press, 1985.

29. Wang, W C. Personal Communication, Bechtel Corporation,San Francisco, CA, 1982.

30. Kuni, D. R. and S. E. Spaid. Coprecipitation of Adipic Acid and Calcium Sulfite Solids. Senior Laboratory Report, The University of Texas at Austin, Department of Chemical Engineering, December 1982.

31. Rochelle, G. T. Buffer Additives for Limestone Scrubbing: A Review of R & D Results. EPRI CS-2897, Vol. 1, pp. 376-436, 1983.

32. Chang, J. C. S., N. Kaplan, and T. G. Brna. Effects of Magnesium and Chloride Ions on Limestone Dual Alkali System Performance. ACS Meeting Preprints, Division of Fuel Chemistry, Vol. 30, No. 2, p. 145-161, April 1985.

33. Laslo, D., J. C. S. Chang, and J. D. Mobley. Pilot Plant Tests on the Effects of Dissolved Salts on Lime/Limestone FGD Chemistry. In: Proceedings: Eighth Symposium on Flue Gas Desulfurization, New Orleans, LA, November 1983, V. 1. EPA-600/9-84-017a (NTIS No. PB84-223031), pp. 424-443, July 1984.

34. Dogliotti, L. and E. Hayon. Flash Photolysis Study of Sulfite, Thiocynate, and Thiosulfate Ions in Solution. J. Phys. Chem. 72: 1800-1807, 1968.

35. Schoeneshoefer, M. Pulsradiolytische Untersuchung ueber das $S_4O_6^{3-}$ -Radaikal als Zwishchenprodukt der Thiosulfatoxidation und Tetrathionatreduktion. Int. J. Radiat. Phys. Chem. 5: 375-86, 1973.

36. Ross, A. B. and P. Neta. Rates of Free Radical Reactions in Aqueous Solution. Nat. Bureau of Standards. June 1979.

37. Davis, E. D., J. B. Louis, and A. Cohen. A Correlation Between the Sulfur-Sulfur Bond Distance and the Activation Energy for a Process Breaking The Bond. J. Am. Chem. Soc. 88:1-6, 1966.

38. Rochelle, G. T. Process Synthesis and Innovation in Flue Gas Desulfurization. EPRI FP-463-SR. July 1977.

39. Foerster, F. and K. Centner. Uber de Einwirkung der Schwefligsuaren Salze auf Polythionate. Z. Anorg. Allgem. Chem. 157:45-82, 1926.

40. Stamm, V. H., O. Seipold, and M. Goehring. Die Reaktionen zwischen Polythionsauren und Schwefliger Saure bzw. Thioschwefelsaure. Z. Anorg. Anorg. Allgem. Chem. 247:277-306, 1941.

41. Fava, A. and G. Pajaro. Cinetique de L'Echange Isotopique Thiosulfate - Trithionate. J. Chim. Phys. 31:594-599, 1954.

42. Foss, O. and I. Kringlebotn. Displacement of Sulphite Groups of Polythionates by Thiosulfate. Acta. Chem. Scand. 15: 1608-1609, 1961.

43. Naito, K., H. Hayata, and M. Mochizuki. The Reactions of Polythionates: Kinetics of the Cleavage of Trithionate Ion in Aqueous Solutions. J. Inorg. Nucl. Chem. 37: 1453-1457, 1975.

44. Nizoguchi, T., Y. Takei, and T. Okabe. Disproportionation of Thiosulfate, Trithionate, Tetrathionate and Sulfite under Acidic Conditions. Bull. Chem. Soc. Jap. 49: 70-75, 1976.

45. Kurtenacker, A., A. Mutschin, and F. Stastny. Uber die Selbstzersetzung von Polythionatlosungen. Z. Anorg. Allgem. Chem. 224: 899-419, 1935.

46. Kurtenacker, A. and M. Kaufmann. Die Zersetzung der Polythionate in Wassriger Losung. Z. Anorg. Allgem. Chem. 148: 43-57, 1925.

47. Rolla, E. and C. L. Chakrabarti. Kinetics of Decomposition of Tetrathionate, Trithionate, and Thiosulfate in Alkaline Media. Environ. Sci. Technol. 16: 852-857, 1982.

48. Goehring, M., W. Helbing, and I. Appel. Die Spontane Zersetzung von Polythionatlosungen. Z. Anorg. Chem. 254: 185-200, 1947.

49. Hofman-Bang, N. Acta. Chem. Scand. 4: 1005, 1950.

50. Foerster, F. and A. Hornig. Zur Kenntnis der Polythionsauren. Z. Anorg. Allgem. Chem. 125: 86, 1922.

51. Stamm, H., M. Goehring, and U. Z. Feldman. Z. Anorg. Allgem. Chem. 250:266, 1942.

52. Swaine, J. W. Thiosulfates. In Encyclopedia of Chemical Technology, 3rd Ed., Wiley-Interscience, Vol. 22, pp.974-989, 1983.

53. Szekeres, L. Analytical Chemistry of the Sulphur Acids. Talanta 21:1-44, 1974.

54. Hartler, N., J. Libert, and A. Teder. Rate of Sulfur Dissolution in Aqueous Sodium Sulfide Solution. Ind. Eng. Chem. Proc. Des. Dev. 6:398-406, 1967.

55. Drum, C. Sodium Sulfides. In Encyclopedia of Chemical Technology, 3rd Ed., Wiley-Interscience, Vol. 21, pp.256-262, 1983.

56. Murin, P. J., T. W. Trofe, and D. A. Dalrymple. Stretford Process Status and R&D Needs. Topical Report by Radian Corporation for the Gas Research Institute, Contract No. 5083-253-0936, 1985.

LIME SLAKING USING STIRRED MILLS

by

N. N. Dharmarajan and R. D. Forbus
Central and South West Services, Inc.
P. O. Box 660164
Dallas, Texas 75266-0164

ABSTRACT

The large tonnages of reagent consumed in lime-based Flue Gas Desulfurization (FGD) processes require that the lime reagent be slaked at the point of use for maximizing economy of operation. The slaking process, which involves mixing the lime with a controlled quantity of water, yields a suspension of extremely fine calcium hydroxide crystals in water.

Slaking is traditionally accomplished using any one of several types of commercially available equipment, such as the ball mill, detention, paste or attrition slaker. The slaker performance and type selected are influenced by a combination of items including lime physical and chemical properties, water quality, installed and operating costs and space availability..

Analysis of commercially available slaking equipment indicated design, operating and maintenance limitations for our spray dryer FGD project. This necessitated our investigation of new methods for slaking lime. The vertical stirred mill appeared to offer several advantages that are desirable. Some of the perceived advantages were simplicity of design, ease of construction, reduced installed cost, ease of operation and maintenance and reduced energy costs.

To evaluate its primary function of producing optimum quality slaked product and also to validate some of the desirable inherent features, a pilot program was conducted to test a vertical stirred mill for possible inclusion in our FGD design.

This paper presents the equipment features and performance results of our pilot evaluation of a vertical stirred mill in lime slaking service. The many desirable features of the vertical stirred mill will be highlighted to support its selection for Coleto Creek Unit 2 Dry FGD lime-based process. Our selection of the stirred mill in lime slaking is the first known use in the United States for a commercial FGD system.

INTRODUCTION

The Cental and South West System serves four states in the South Central United States. Central and South West Corporation includes four operating electric utilities: Central Power and Light Company, Public Service Company of Oklahoma, Southwestern Electric Power Company and West Texas Utilities (Figure I). The total system generating capacity is 12,200 MW.

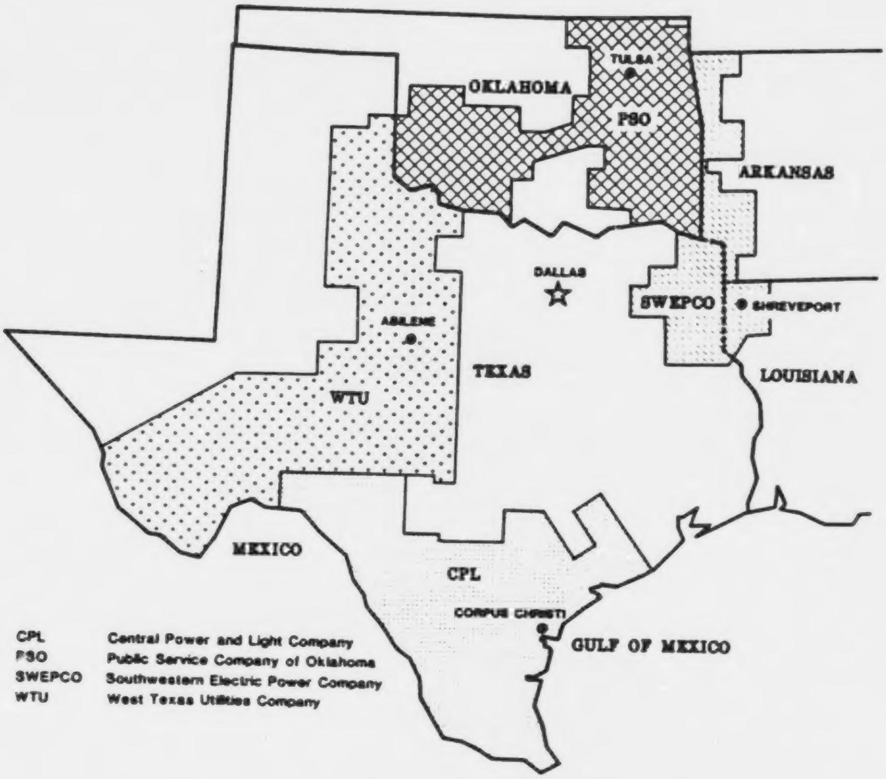

TULSA
OKLAHOMA
PSO
ARKANSAS
DALLAS
SWEPCO
SHREVEPORT
ABILENE
TEXAS
LOUISIANA
WTU
MEXICO
CPL
CORPUS CHRISTI
GULF OF MEXICO
CPL Central Power and Light Company
PSO Public Service Company of Oklahoma
SWEPCO Southwestern Electric Power Company
WTU West Texas Utilities Company

FIGURE I. CENTRAL AND SOUTH WEST SYSTEM.

Central Power and Light Company's Coleto Creek Power Station is located near Victoria, Texas. Unit 1 is a 609 MW (net) coal fired generating station that began commercial operation in 1980. Plans for a second unit were developed in the summer of 1980, with commercial operation scheduled in a window between 1988 and 1992. The unit size is to be 726 MW (gross). Low sulfur sub-bituminous coal will be utilized as the fuel.

Unit 2 will include an FGD system to satisfy EPA'S New Source Performance Standards. Extensive studies and detailed design evaluations led to the selection of a lime-based spray dryer FGD process in 1983 for Unit 2's gas clean-up operation.

LIME AND LIME SLAKING BASICS

LIME

Calcium oxide (CaO) is produced by calcining limestone (calcium carbonate ($CaCO_3$)) at high temperatures in a kiln. Its chemical and physical characteristics are affected by several factors.

The primary factor is the lime's calcium content. This can vary from as low as 50% in a dolomitic (high magnesium) lime to over 95% in a high calcium lime. The calcium content is a natural characteristic of the original limestone and will vary from one quarry to another. The non-calcium part of the lime is generally composed of silica, alumina, magnesia, iron oxide, and fragments of kiln brick. The high calcium limes used for FGD have a minimum of these inert components and a maximum amount of the more desirable calcium oxide.

Calcination temperature is another important parameter. The kiln used to fire the limestone may be operated at different temperatures and calcining durations. However, the time and temperature used must be such as to allow complete conversion of the calcium carbonate to calcium oxide without fusing the porous calcium oxide into a glassy "dead burned" state. The type of lime most commonly used in the spray dryer FGD process is the highly reactive "soft burned" type.

LIME SLAKING

The hydration of lime to form calcium hydroxide (also known as hydrated or slaked lime) in the presence of excess water by the exothermic reaction

$$CaO\ (s) + H_2O\ (l) = Ca(OH)_2 + 27{,}500\ \text{BTU/Lb-mole}$$

is called slaking. When properly slaked, the result is a suspension of extremely fine calcium hydroxide crystals in water. This small particle size is important because the chemical reaction of lime with SO_2 occurs on the surface of these crystals. Smaller crystals have more surface area and thus will react more quickly. A soft burned pebble lime will rapidly disintegrate in an explosive chain reaction to produce a slurry of extremely fine (1 to 3 micron) suspended slaked lime particles . Typical reaction time for a good quality lime is 5 to 10 minutes (ASTM C110 Lime Reactivity test).

The hydration reaction generates a considerable amount of heat. The final temperature of the slurry is controlled by varying the amount of excess water present in the mixture. Best results are indicated by temperature rise to about 170 to 190 F with water-to-lime ratios of 2.5 to 4.0.

Under ideal conditions, all the of the calcium oxide is converted to very fine (minus 325 mesh) calcium hydroxide slurry. The inert material in the lime does not react and is still present in the slurry as particles from -325 mesh to the feed top size. The non reactive "grit" also contains some unreacted limestone and unreacted lime. This grit material is much more abrasive than the fine calcium hydroxide particles unless it is ground up or removed from the slurry before passing on to the downstream process. One method of avoiding excess equipment wear is to separate the grit from the lime.This can present practical problems when large tonnages are involved.

Hydration and degritting are performed using special processing equipment known as slakers. Slakers perform the function of mixing controlled amounts of water and lime to generate a calcium hyroxide slurry. The slurry is then processed to remove grits. Slakers generally require auxiliary equipment to perform the grit separation or classification. An ideal situation exists when the mill performs both the slaking and grit grinding steps at the same time. This offsets the abrasive characteristics of the grits without separate degritting and at the same time exposes unreacted lime tied up with the grits for further hydration. Many different slaker designs are available but for large quantity processing the ball mill slaker has found wide acceptance.

PILOT PLANT DEVELOPMENT BACKGROUND

Our process design includes an absorber feed preparation step which requires blending the slaked lime with recyled waste FGD solid byproduct. This process step is required to optimize drying, enhance lime utilization and offset any scaling possibilities. In reviewing the process needs to support the successful recycle operation and for the favorable kinetics of the chemical reaction of lime with the SO2, it was evident that the slaked lime particles had to be consistently less than 5 microns in size.

The Dry FGD process supplier's design recommendation was to use a ball mill slaker with continuous production of slaked lime. This was in lieu of batch production, which was preferred both operationally and from a product quality standpoint. The considerations for the vendor's continuous operation recommendation were:

1) Each time the ball mill is started up, inefficient slaking will occur until the mill load is optimized (correct percent solids throughout the mill) and the proper slaking temperature (grinding media, mill lining and lime milk) is reached. Therefore, batch operation was deemed to result in inefficient use of the lime available for slaking.

2) The mill drive train components (starter, motor, drive couplings, pinion shaft and gear) will experience increased wear

and tear during initial start-up. Reducing or limiting the frequency of starting/stopping will reduce the probability of failure of the drive train components.

3) Each time the mill is shut down, it must be cleaned and flushed. Operating in a continuous mode will decrease both the operator time and the quantity of wash water that must be handled.

Basic to our concern was the turndown limitation of ball mill slakers in continuous operation. Pilot tests and verification on commercial size units indicate inconsistent slaked product quality at feed throughputs below 70% of the mill's design capacity. For our application, the varying heat input to the boiler and the wide range of fuel sources (varying sulfur levels) being considered led us to question the performance capability of ball mills.

From an operational standpoint it was desired to keep mechanical components such as mill auxiliaries and grits handling to a minimum so that operating reliability and reduced maintenance could be achieved. Our search of different options indicated the applicability of the vertical stirred mill was in keeping with our design objectives. However, no data was available to attest to the stirred mill's use as a slaker. This resulted in a pilot program to test the mill's applicability in lime slaking.

SCOPE OF THE PILOT PLANT TEST

The primary objectives of the pilot plant program were to run parametric tests to validate the stirred mill's performance as a slaker and to verify other attributes such as power needs, noise levels,etc.

The test matrix included the following:

a) varying lime feed rate
b) varying water quality and temperature
c) varying lime quality
d) varying lime-to-water ratio

The matrix selection was to ascertain:

a) the stirred mill's turndown capability
b) acceptability of poor quality waste water
c) need for pre-heating inlet water to support product quality
d) disposition of grits
e) effect of higher amounts of magnesium in lime
f) maximum lime-to-water ratio which would offset the need for downstream dilution and hence not require a stabilization tank and its associated auxiliaries such as agitator, pumps and controls.

DESCRIPTION OF EQUIPMENT

The generic stirred mill (Figure II) consists of a stationary vertical cylindrical shell which is supported on three legs. A spiral agitator or screw is overhung inside from the drive assembly. The screw is driven by an overhead mounted motor through a gear reducer.

The space between the screw and the shell is filled with steel balls. These balls are agitated when the screw rotates and they circulate freely both vertically and radially. The weight of the ball charge and the screw help position the rotating shaft and offset the need for guide bearings at the bottom.

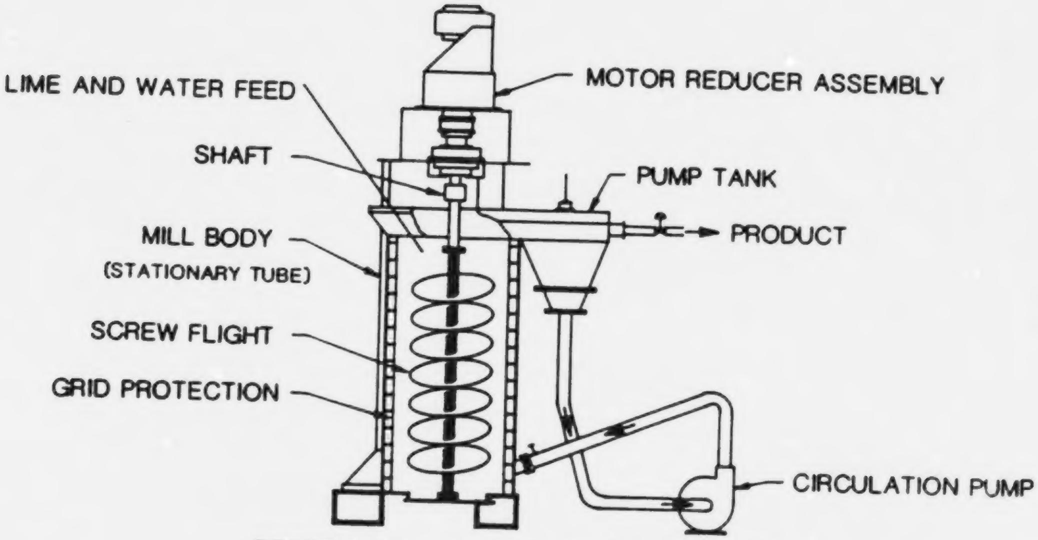


FIGURE II. STIRRED MILL DETAILS.

The stationary cylinder is protected against wear by a grid assembly which serves to trap the ball media, thereby forming a wearing surface of media against media. The stationary cylinder and the grid assembly are made of steel. The screw flights are constructed of Ni-Hard and are replaced by bolting to the shaft collars.

For the slaking application, the top portion of the screw shaft includes an agitator blade to disperse and mix the incoming lime feed. The lime to be slaked and water will be introduced from the top and fall by gravity into the mill body. A hood mounted over the top will be connected to a steam scavenger system to preclude lime feed chute pluggage.

MILL OPERATION

During operation, the mill is fed controlled amounts of fresh pebble lime and water. The rotating screw flights agitate the ball charge which grinds the lime, exposing fresh surfaces for hydration. The size reduction is accomplished by a combination of ball-to-ball, ball-to-screw and pebble-to-pebble attrition. The finely hydrated lime particles are carried upward through the chamber and overflow into a pump tank.

A mill circulating pump reintroduces the product into the bottom of the mill in a closed circuit. The pump circulation rate is selected to provide a velocity through the mill body so as to increase the probability of ball/lime contact. This controlled circulation acts as a grit trap and tends to retain oversize material in the mill until it is finally reduced to the correct size. A bleed stream from the pump tank is fed directly into the process based on demand. The circuit does not include any degritting step.

The hydration reaction generates a considerable amount of heat. The final temperature of the slurry is a function of the amount of excess water above the stoichiometric requirement. To protect against a loss of water flow and guard against overheating and possible explosion, temperature sensors planted in the mill body will activate an emergency inlet water valve.

TEST MILL DETAILS

Characterization tests were performed using a laboratory size mill rated at a design capacity of 600 pounds per hour and subsequent tests were run using a prototype mill sized to match the design lime needs for our full scale installation (3.2 tons per hour). Table I presents the equipment information for the two mills tested.

TABLE I. STIRRED MILL DETAILS.

	LABORATORY SIZE	PROTOTYPE
Overall Height	14'-0"	21'-0"
Grinding Chamber Height	6'-6"	9'-9"
Ball Height in Chamber	5'-6"	4'-6"
Inside Grid Diameter	15.375"	26.75"
Motor HP	5	20
Weight of 1" balls	none	2358 lbs.
Weight of 3/4" balls	2315 lbs.	2142 lbs.
Screw speed	82 RPM	82 RPM

TEST OPERATING CONDITIONS

Screening tests with the laboratory size stirred mill were performed using lime-to-water ratios corresponding to an approximate final solids concentration of 15 to 17 %. Subsequent testing with the prototype stirred mill was effected using a lime-to-water ratio to yield an approximate final solids concentration of 25%. This ratio was based on the process material balance with regard to the quantity of water that could be introduced with the lime slurry. The water was not preheated and averaged about 11 C (52 F) for the small mill tests and 25 C (77 F) for the prototype test runs. The lime feed rate was varied between 2% and 120% of the design rates for the small mill while the prototype mill test feed rate was varied between 10% and 100% of design capacity. Table II presents the details of the test matrix.

TABLE II. TEST MATRIX INFORMATION

Mill type	Laboratory Size	Prototype
Mill rating	600 lbs/hr	6400 lbs/hr
Product % Solids	15% - 17%	22% - 25%
Throughput rates	2% - 120%	10% - 100%
Water temperatures	11 C	25 C

LIMES TESTED

Both mills were tested with a high calcium, soft burned pebble lime with about 5% inerts (composed of silica, alumina, hematite, and magnesia). Additionally, the prototype mill was also tested with a pebble lime containing 5% magnesium oxide. Table III presents the chemical and physical analyses of the two limes. The criteria for the lime selection was to match the process design basis in terms of available calcium oxide (CaO) and grit content. The testing of the high magnesium lime was for comparison to the high calcium reagent.

TABLE III. LIMES TESTED IN MILLS

	Lime I	Lime II
Total CaO (as CaO)	94.0	90.3
% Avail. CaO	92.3	86.7
% MgO	1.5	5.0
% Grits	5.0	9.7
Size (inches)	5/8 x 0	1 x 0
3 Min. temp. rise	51.5 C	44 C
Active slaking time	2.5 min.	4.5 min.
Total temp. rise	51.5 C	51 C
Initial Water temp.	25 C	25 C

SLAKING WATER QUALITY

Table IV presents the composition analysis of the water used for slaking.

TABLE IV. SLAKING WATER ANALYSIS.

	Water I		Water II	
	(1)	(2)	(1)	(2)
Ca++	15 PPM	37 PPM	15 PPM	37 PPM
Mg++	5 PPM	20 PPM	5 PPM	20 PPM
Na+	6 PPM	13 PPM	1231 PPM	2684 PPM
SO4=	22 PPM	22 PPM	2590 PPM	2694 PPM
Cl=	15 PPM	21 PPM	15 PPM	21 PPM
HCO3=	33 PPM	27 PPM	33 PPM	27 PPM
TDS		70 PPM		2742 PPM
pH	7.7		7.7	
SS	<1 PPM		<1 PPM	

(1) Reported as ion
(2) Reported as equivalent CaCO3

While most tests were performed using Water I, there were several runs with the prototype mill, where the slaking water was dosed with sulfate compounds to simulate ash pond quality water.

DISCUSSION OF RESULTS

The performance evaluation for characterizing the mill product was predicated on the following:

- Wet screen analysis of samples
- Solids settling rate
- Microscopic examination of grits
- Particle size count
- Available lime index

Samples from the different test runs listed in TABLE II were collected after the mill had attained steady state conditions as evidenced by constant temperature of the product stream. The samples were analyzed for solids content to ensure compliance with operating conditions.

WET SCREEN ANALYSIS OF SAMPLES

Table V presents the screen analyses for the stirred mill product. Included in the table, for comparison purposes, are screen analyses for ball mill slaked lime samples.

TABLE V. WET SCREEN ANALYSIS OF PRODUCT

Mill Type	BALL MILL		STIRRED MILL	
% Design feed rate	50 %	40%	100 %	2 %
Mesh Size	Cum %	Cum %	Cum %	Cum %
35	0.00	0.00	0.00	0.00
40	0.00	0.00	0.20	0.10
60	1.30	2.18	0.00	0.00
65	0.00	0.00	0.50	0.00
100	3.25	7.25	0.80	0.00
150	0.00	0.00	1.40	0.30
200	5.85	11.60	2.10	0.50
270	0.00	0.00	2.80	0.80
325	11.05	21.03	3.20	1.00
-325	88.95	78.97	96.80	99.00

The percentage of +100 mesh grit increases from 3.25% to 7.25% as the ball mill feed rate is decreased, in comparison to a decrease in the grit content from 0.8% to 0.10% with feed turndown in the stirred mill. This indicates that the stirred mill performance gets better with turndown and the ball mill product deteriorates at reduced rates. It thus appears that the ball mill should be run at full capacity for optimum performance.

Figure III presents the particle size distribution of products from the small stirred mill and a ball mill at different lime feed rates. The stirred mill feed rate was varied between 2% and 120% of the design throughput with the ball mill rate turndown to 40 % of its design value.

The stirred mill performance improved with feed rate turndown as depicted by the lower cumulative weight percent retained on larger mesh screens. By comparison, the cumulative weight percent retained on larger mesh screens increases with feed rate turndown for a ball mill. Thus, the stirred mill appears to be very effective at reducing the grit particles in the lime,thereby insuring no hide-outs (unslaked lime) and wastage of lime.

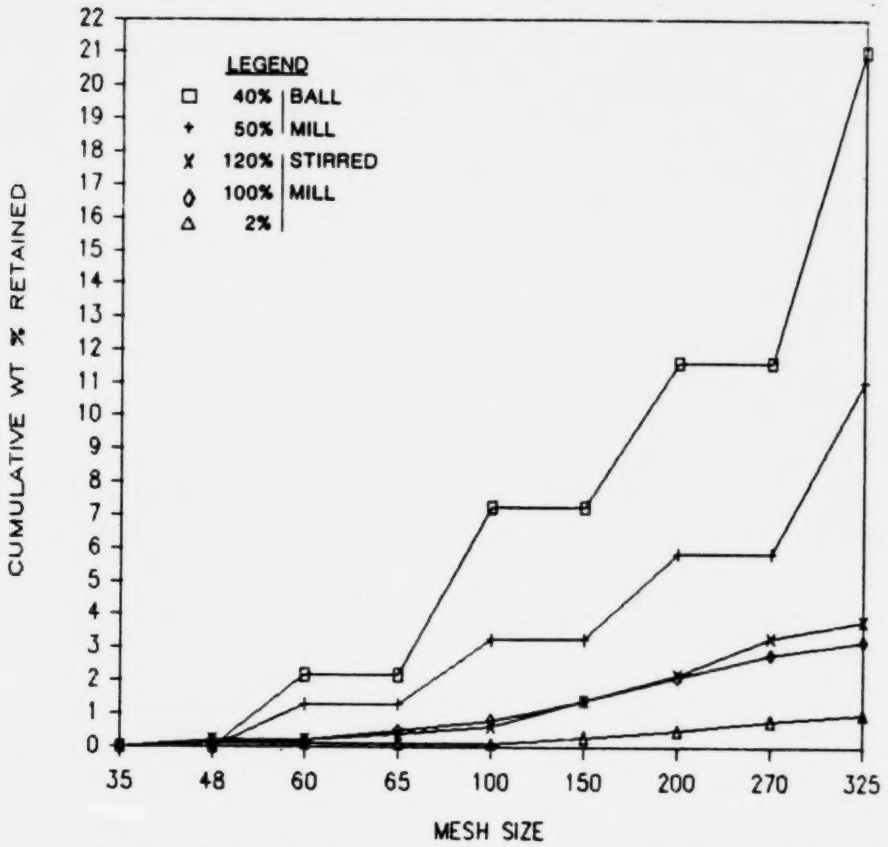


FIGURE III. PARTICLE SIZE DISTRIBUTION COMPARISON

An interesting observation was the effect of the slaking water temperature on the stirred mill product screen analyses. The inlet slaking water was at 11 C (52 F) and the stabilized product temperature was about 44 C (102 F). At the turndown and design conditions the effect of the lower water temperature and higher rates did not seem to effect the slaked lime quality. This seems to raise the question about the importance of temperature as a yardstick for measuring a slaked product quality.

SOLIDS SETTLING RATE

Figure IV compares the settling rates between the stirred mill and ball mill products, at varying lime feed rates. These results are for a product solids concentration (as slaked) of about 17%.

The stirred mill settling characteristics are depicted only for the 100 % feed rates because at reduced throughputs the solids in the slurry were too fine to settle. The comparison attests to a good product quality with the stirred mill, based on settling rate characteristics as a product quality yardstick.

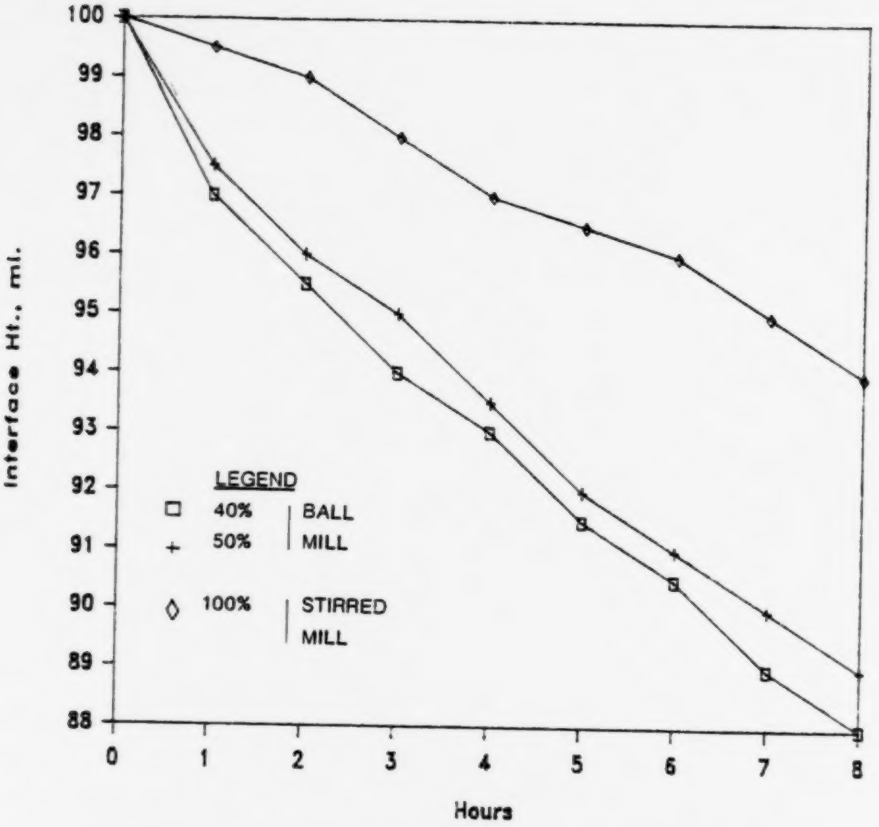


FIGURE IV. SOLIDS SETTLING RATE COMPARISON.

Figure V shows the ASTM settling rate tests, where the stirred mill product diluted to 10% solids slurry is compared with a similar quality slurry from a ball mill. The pronounced effect of the fineness of the stirred mill product is demonstrated by the slower settling rate compared to the ball mill. This test method presumably discriminates changes in slaked lime quality much more readily, by offsetting interference problems usally encountered with concentrated slurries.

To further support the effectiveness of the slaking and ascertain no lime hide-out in the grits, samples of the stirred mill product were collected during the different test runs for analysis a few weeks later. Within limits of error,as presented in Table VI, the sieve analysis on the aged product was comparable to the analysis done on the freshly collected samples, suggesting completeness of the slaking reaction. The stirred mill, when sampled at about 120% of its design capacity, yielded a higher fraction of +325 mesh material compared to an aged sample at the same 120% throughput. However, the overall fineness of the product

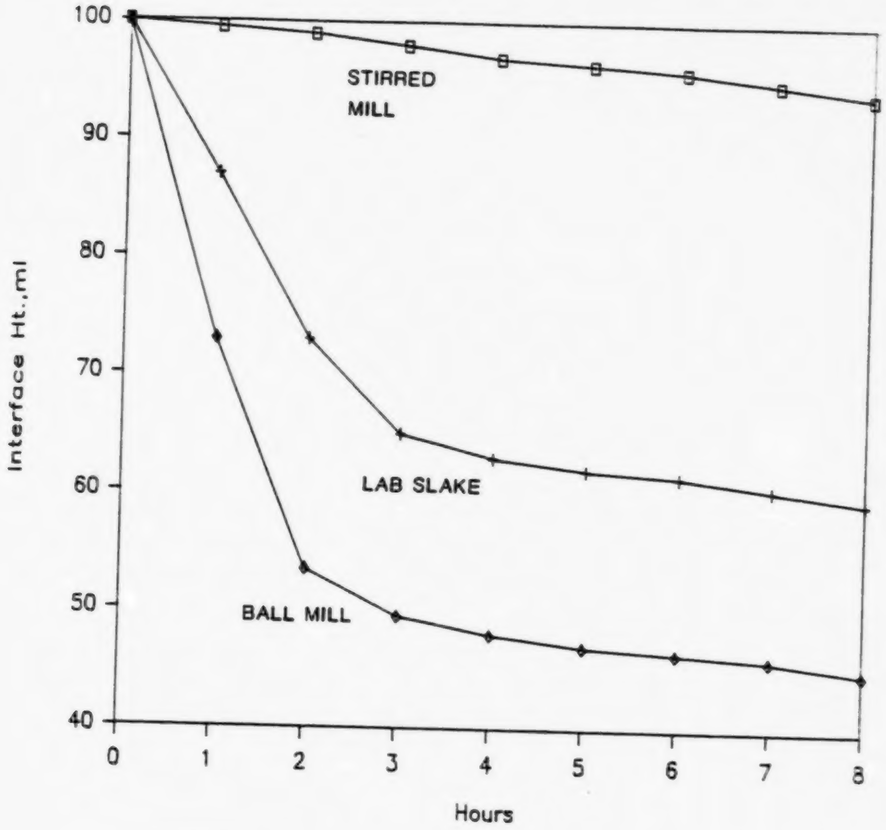


FIGURE V. ASTM SETTLING TEST COMPARISON.

TABLE VI. AGING EFFECTS ON SLAKED PRODUCT.

% Design feed	2 %		100 %		120 %	
Mesh Size	Cum % (1)	Cum % (2)	Cum % (1)	Cum % (2)	Cum % (1)	Cum % (2)
35	0.00	0.00	0.00	0.00	0.00	0.00
48	0.10	0.00	0.20	0.20	0.20	0.30
60	0.00	0.00	0.00	0.00	0.00	0.00
65	0.00	0.00	0.50	0.50	0.40	0.00
100	0.00	0.20	0.80	0.80	0.60	0.90
150	0.30	0.00	1.40	1.20	1.40	0.00
200	0.50	0.40	2.10	2.00	2.20	1.40
270	0.80	0.60	2.80	2.70	3.30	1.80
325	1.00	0.90	3.20	3.00	3.80	2.20
-325	99.00	99.10	96.80	97.00	96.20	97.80

(1) screened 5 minutes after sampling
(2) screened 2 weeks after sampling

was superior to that of a ball mill at 100% of its design lime feed rate.

MICROSCOPIC EXAMINATION OF SOLIDS

Microscopic examination of the solids material validated the physical findings. The different materials could be identified by their distinct colorations; i.e. clear (silica), brown (limestone), black (coal or iron ore), opaque white (CaO), and white porous balls (hydrated lime, $Ca(OH)_2$).

The samples for the stirred mill high turndown situations consisted of mostly white porous balls, with traces of small grit particles in various colors and irregular shapes. The grit particles were as small as the hydrated lime. The stirred mill sample collected under the turnup situation (120% case) contained irregular grit material imbedded with white lumps (presumably unslaked calcium oxide).

PARTICLE SIZE ANALYSIS

Sedi-Graph analysis of the stirred mill hydrated lime particles are shown in Table VII for various lime feed rates. The data for the 80 % and 50 % cumulative mass percent shows particle size to be less than 2.6 microns, indicating optimum size for favorable reaction kinetics. Additionally, these findings seem to suggest that if the stirred mill is operated within its maximum design rating, no auxiliary grit collection or grit screening would be required. Grit handling has been required in other types of slakers, with attendant maintenance, disposal and reagent wastage problems.

TABLE VII. PARTICLE SIZE COUNT.

% Design feed rate	120%		100%		50%	
Cumulative Mass %	80%	50%	80%	50%	80%	50%
Particle Size, Microns	2.60	2.25	2.25	2.10	2.15	2.00

AVAILABLE LIME INDEX

The available lime index, which indicates the percentage of the slaked product solids present as calcium hydroxide, was calculated for the stirred mill samples (ASTM C-25 Test).

The percent solids in the mill product was in the range of 22% to 25%. The calculated available lime index varied between 94% and 96% for feed rate turndown from 100% to 10 % of design. This positive improvement with feed rate turndown is more favorable than a ball mill where the available lime index exhibits a downward trend with feed rate turndown. Additionally, the high available lime index suggests a high conversion of the oxide to the hydroxide form. The maximum available lime index for a ball mill slaking similar quality lime at design lime feed rates is reported at 92 %.

WATER AND LIME QUALITY EFFECTS ON STIRRED MILL PERFORMANCE

Figure VI shows the effects of the lime and water quality on the stirred mill performance as measured by the particle size distribution criteria. In these test runs the feed rates were varied between 11 % and 100 % of design .

The tests involved using the 5% MgO Lime II and the higher sulfates Water II. The effect of the high levels of sulfates (2590 PPM) in the water is very pronounced at the design lime feed rates, as shown by the higher weight percent retained on the 325 mesh and larger screens. This finding supports data of other slakers.

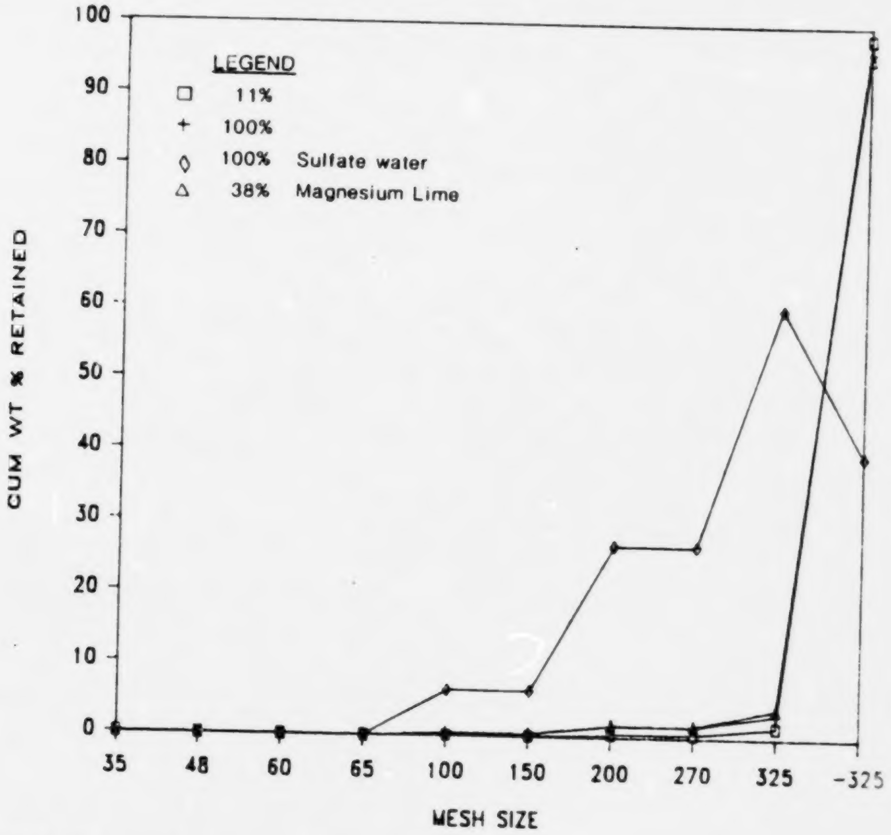


FIGURE VI. EFFECT OF LIME AND WATER QUALITY ON MILL PERFORMANCE

High magnesium lime (5% MgO) was tested at feed rates corresponding to 38% of the mill design capacity. This test indicates a slight change in the product quality but the grind is finer than what might be expected from a ball mill. Available lime index determination for the slaked product supports the slaking characteristics of this lime. The available lime index was lower in comparison to the tests with Lime I and averaged 90%.

MISCELLANEOUS OPERATING CHARACTERISTICS

NOISE LEVELS

Sound readings were taken approximately three feet from the prototype mill with the instrument positioned 90 degrees to the source. These readings were taken at different lime feed rates and at different elevations. The highest readings were recorded at the top elevation near the motor. The maximum reading registered was 85.5 dbA. It appears that the stirred mill will satisfy OSHA standards without the need for sound attenuation.

POWER REQUIREMENTS

Power needs were monitored for different lime feed rates and product solids concentrations. The net HP-HR/TON of lime showed a decrease with increasing solids concentration, as presented in Table VIII, for the stirred mill design lime feed rates (100 % capacity). High solids slurry operation (within limits) should thus allow optimum usage of power. Ball mill slakers are projected to consume more power with increasing solids concentration because of the high viscosity effects on the ball lifting operation and hence more torque.

TABLE VIII. NET POWER FOR DIFFERENT SOLIDS CONCENTRATION FOR THE STIRRED MILL AT 100% FEED CAPACITY

% Product solids	Net HP-HR/TON
26	6.6
22	7.6
20	8.0
13	9.1

In terms of gross power consumption, the stirred mill with its stationary shell offers considerable savings in energy in comparison to a ball mill where a sizable amount of power for processing is expended in rotating the shell and lifting the balls.

The favorable slaking characterstics, as indicated by the aging tests, would appear to offset the need for a downstream stabilization tank and its complement of agitator, pumps, controls etc. The stirred mill should permit direct metering of the product into the process thereby affording simplicity of design and reduced operating and maintenance expenses.

SUMMARY

The analysis of the test results seemed to validate the stirred mills capability as a slaker. In particular the following process related features are noteworthy:

1. The capability of the mill to produce very fine particles of slaked lime under turndown conditions suggests continuous operation possibilities with attendant reduction in mill size.

2. The fine particle sizes should enhance reagent utilization and SO_2 removal.

3. The effectiveness of the mill in reducing grits to fines without the need for separate degritting should permit simple operation and maintenance and also guard against lime wastage with the grits. The effective grit grinding should result in less lime hide-out and, most importantly, reduce erosion of the downstream processing equipment.

4. Lower temperature inlet water does not seem to effect slaking, thereby offsetting the need for preheating to support a quality product.

5. The advantage of decreased net power consumption at higher solids concentrations and completeness of slaking within the mill circuit should offset the need for a downstream hold tank and its associated agitator, pumps, instrumentation and controls. This will provide savings in capital, operating and maintenance expenses.

6. The available lime index, which is an indicator of the hydration effectiveness, suggests higher conversion for the stirred mill in comparison to a ball mill. Additionally, the available lime index shows improvement with feed rate turndown which is absent in ball mill slakers.

Aside from the favorable process results, the stirred mill offers numerous practical advantages over a ball mill. Some of these are:

1. The stirred mill with its vertical configuration would require floor space about a third that of a ball mill sized for the same design duty. This consideration was important in our application where a second unit must be built in very limited space.

2. The foundation requirements are simple and smaller.

3. Assembly and erection would be easier considering the absence of big bull gears and trunnion bearings, which are typical of ball mills.

4. A stirred mill is devoid of auxiliaries like high-lift pumps (used in ball mill start-up), spray lube system and bearing cooling water. This should facilitate operation and maintenance.

5. Most importantly, the total cost comparison for a duty similar to our application is revealing. The installed cost for the stirred mill was 40% lower than a comparable ball mill system. This comparison did not include the capital and installation costs for the holding tank, agitator and pumps that would be associated with the ball mill system.

6. The sizable reduction in gross power usage in comparison to a ball mill is a significant operating cost consideration. The power savings for the stirred mill (including the recirculation pump) compared to a ball mill in similar duty was estimated at 42 %.

7. Material cost comparisons for wear items based on estimated annual replacement indicated savings of 15 % for the stirred mill.

CONCLUSIONS

The project saw the advantages of the stirred mill in meeting the process criteria as a slaker as well as other benefits such as reduced capital, operating and maintenance costs. These desirable attributes resulted in the inclusion of the stirred mill slaker in our Coleto Creek 2 spray dryer FGD plant.

Note: The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not reflect the views of the Agency and no official endorsement should be inferred.

LIMESTONE SELECTION AND PREPARATION FOR FGD

By: Dorothy Stewart
Electric Power Research Institute
Palo Alto, California 94303

J. David Colley
Radian Corporation
Austin, Texas 78766

O. W. (Buddy) Hargrove
Radian Corporation
Austin, Texas 78766

A. J. Jones
Radian Corporation
Austin, Texas 78766

ABSTRACT

Limestone properties and preparation for conventional wet scrubbing flue gas desulfurization systems have been investigated in the laboratory and pilot plant with some full-scale tests for comparison. Major factors affecting limestone performance are the pH of the scrubber liquor and the particle size distribution of the limestone. Utilization of the reagent is above 90% when the stone is ground to >90% passing through 325 mesh. To accomplish this grinding, the wet ball mill and tower mill have the greatest efficiency and lowest system cost. Because of the decreased requirement for -325 mesh limestone, a system to grind to 90% -325 mesh is less costly then a system producing only 80% -200 mesh. Limestone tests at the Duck Creek station of Central Illinois Light Co. show that two of the stones tested are less expensive to use than current supply and can maintain desired SO_2 removal. Laboratory evaluation of these limestones did not completely define their behavior at full scale.

INTRODUCTION

In flue gas desulfurization systems using limestone as reagent, the utilization of limestone depends on the limestone selected and the preparation of the limestone. In many cases, the properties of the limestone slurry feed to the wet scrubbing system can have great influence on the operation of the entire system. Previous laboratory and pilot plant data have shown that limestone particle size and composition affect the rate of limestone dissolution under a given set of operating conditions. In addition, this rate is affected by operating conditions such as liquor composition, pH, agitation, and retention time. While there are laboratory tests that give some indication of the performance of a limestone, there are few studies on the commercial scale to relate reagent slurry properties to performance. This paper presents results of laboratory, pilot plant, and commercial scale studies of limestone selection and preparation.

LABORATORY AND PILOT PLANT RESULTS

FACTORS AFFECTING LIMESTONE DISSOLUTION

Laboratory studies of limestone dissolution have shown that the FGD variables having a major effect on limestone reactivity are pH and limestone grind (i.e., particle size). The effect of pH on dissolution of $CaCO_3$ and $MgCO_3$ from limestone containing varying quantities of $MgCO_3$ is shown in Figure 1. The lower the pH the greater the rates of solution of both calcite ($CaCO_3$) and dolomite ($CaCO_3 \cdot MgCO_3$) but the magnitude of the change varies for the different limestones. At a given pH, a decrease in particle size increases the rates of solution, particularly of limestones that are mostly calcite, having low levels of $MgCO_3$ (Figure 2). Operating conditions such as temperature and degree of agitation have an effect on rate of solution; however, these conditions are relatively constant in FGD systems and are not used to alter limestone utilization.

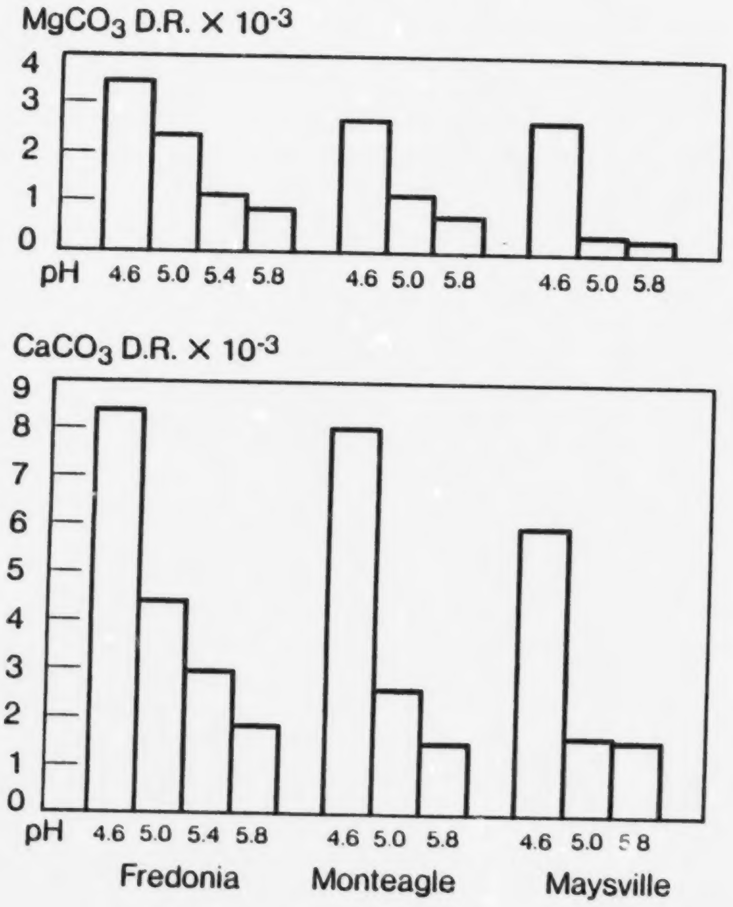


FIG. 1. EFFECT OF pH ON LIMESTONE DISSOLUTION

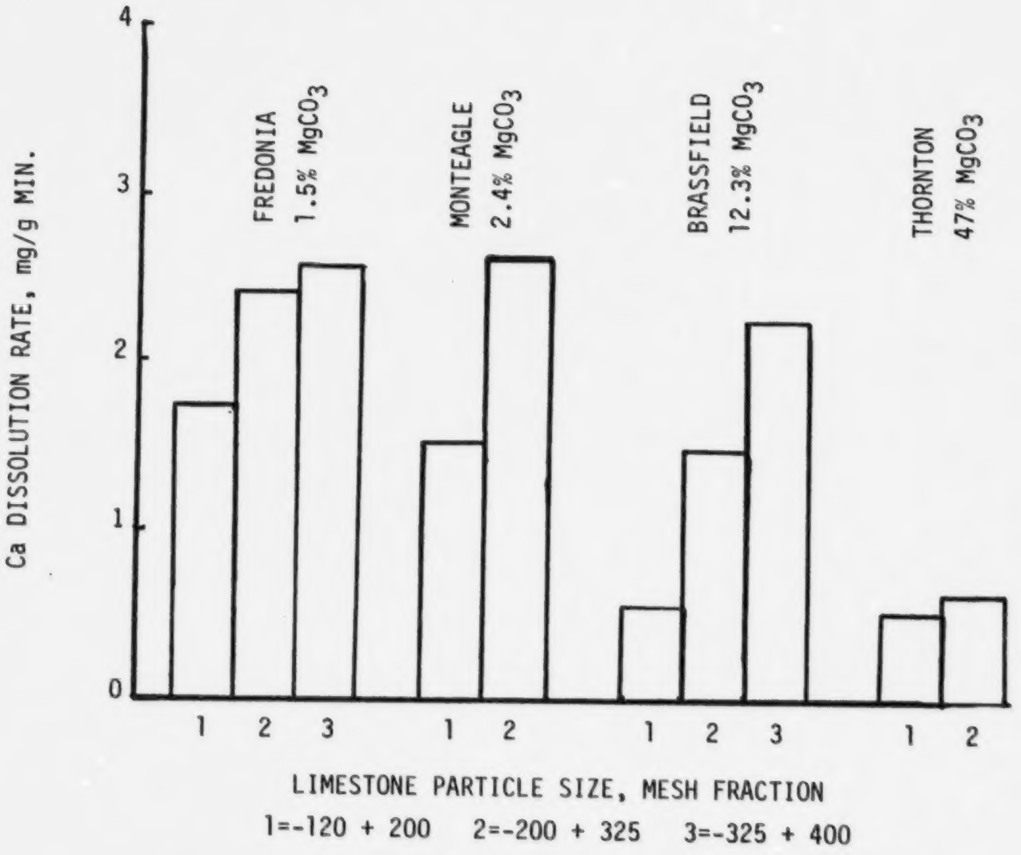


FIG. 2. EFFECT OF PARTICLE SIZE ON LIMESTONE DISSOLUTION

Because altering particle size is a relatively easy means of increasing the rate of limestone dissolution, a study was made of grinding limestone in five milling circuits: open circuit wet ball mill, closed circuit wet ball mill, hammermill, tower mill and ring roller mill. The energy required to grind to various particle size ranges and the effect of particle size on the rate of dissolution are shown in Table 1 and 2.

TABLE 1. EFFECT OF PARTICLE SIZE ON MILL ENERGY

Limestone	Product Size % -200 mesh	 % -325 mesh	Specific Energy, hp - hr/ton
Kimmswick			
Wet Ball Mill (Closed Circuit)	90	ND	12
	98	ND	15
Tower Mill	93	65	6
	100	88	11
Hammer Mill	81	ND	31
	99	ND	27
Ring Roller Mill	49	ND	30
	61	ND	87
Monteagle			
Wet Ball Mill (Closed Circuit)	90	ND	15
	98	ND	20
Tower Mill	97	70	10
	99	85	14
Hammer Mill	78	ND	43
	98	ND	47
Ring Roller Mill	37	ND	45
	57	ND	105

TABLE 2. EFFECT OF MILL TYPE AND PARTICLE SIZE ON LIMESTONE DISSOLUTION RATE

Limestone	Mill	Mesh Size	Ca Dissolution Rate, mg/g min
Kimmswick	Wet Ball Mill	- 200 + 325	-
		- 325 + 400	5.2
	Tower Mill	- 200 + 325	3.7
		- 325 + 400	5.3
Monteagle	Wet Ball Mill	- 200 + 325	3.6
		- 325 + 400	5.2
	Tower Mill	- 200 + 325	3.8
		- 325 + 400	5.3

The Kimmswick limestone is the softer stone with a Bond Work Index of 7, and Monteagle is a hard stone with a Bond Work Index of 12. With both stones, the energy requirements for grinding to a given particle size are the lowest for the closed circuit wet ball mill and the tower mill. As expected, the harder stone (Monteagle) has a slightly higher energy requirement. The grinding equipment does not appear to affect the dissolution rate of limestone of equivalent particle size (Table 2). However, the rate does increase significantly with decreasing particle size of the limestone.

The increase in dissolution rate of limestone of finer grind may compensate for the increase in energy required to grind to the finer size. In order to determine the relationship between limestone particle size and limestone utilization, data from the EPRI Chemical Process Problems Project at the Duck Creek station of Central Illinois Light Company (CILCo) were reviewed to establish a commercial value for use in estimating cost of grinding. The data are summarized in Table 3.

TABLE 3. EFFECT OF LIMESTONE PARTICLE SIZE ON LIMESTONE UTILIZATION IN A COMMERCIAL FGD SYSTEM

Kimmswick Limestone, Particle Size		Limestone Utilization
% -200 mesh	% -325 mesh	at 5.8 pH, %
86	70	58
94	81	89
99	90	92

REAGENT PREPARATION SYSTEM COSTS

Using the data from the Duck Creek station and from the pilot grinding studies, cost estimates were prepared for limestone reagent preparation systems using each of the mills tested. Cost were developed for a 500 MW plant using high sulfur coal with limestone size specifications of 80% -200 mesh and 90% -325 mesh, Figure 3. Because of the lower energy requirements of the wet ball mill and tower mill, preparation systems using these mills are less costly than those using the other mills. For both the ball mill and tower mill systems, the finer grind (90% -325 mesh) lowers the cost of the system because of the reduced quantity of limestone required resulting from greater utilization.

The hardness of the limestone can also affect the cost of a preparation system. Additional test with the two least costly mill systems were completed with several limestones ranging from 6 to 12 in Bond Work Index. Figure 4 shows the effect of limestone hardness on costs of these two systems. For the softer stone (Bond Work Index of 6) the two mill systems are about the same cost. However, the tower mill is less costly than the ball mill for the harder limestones.

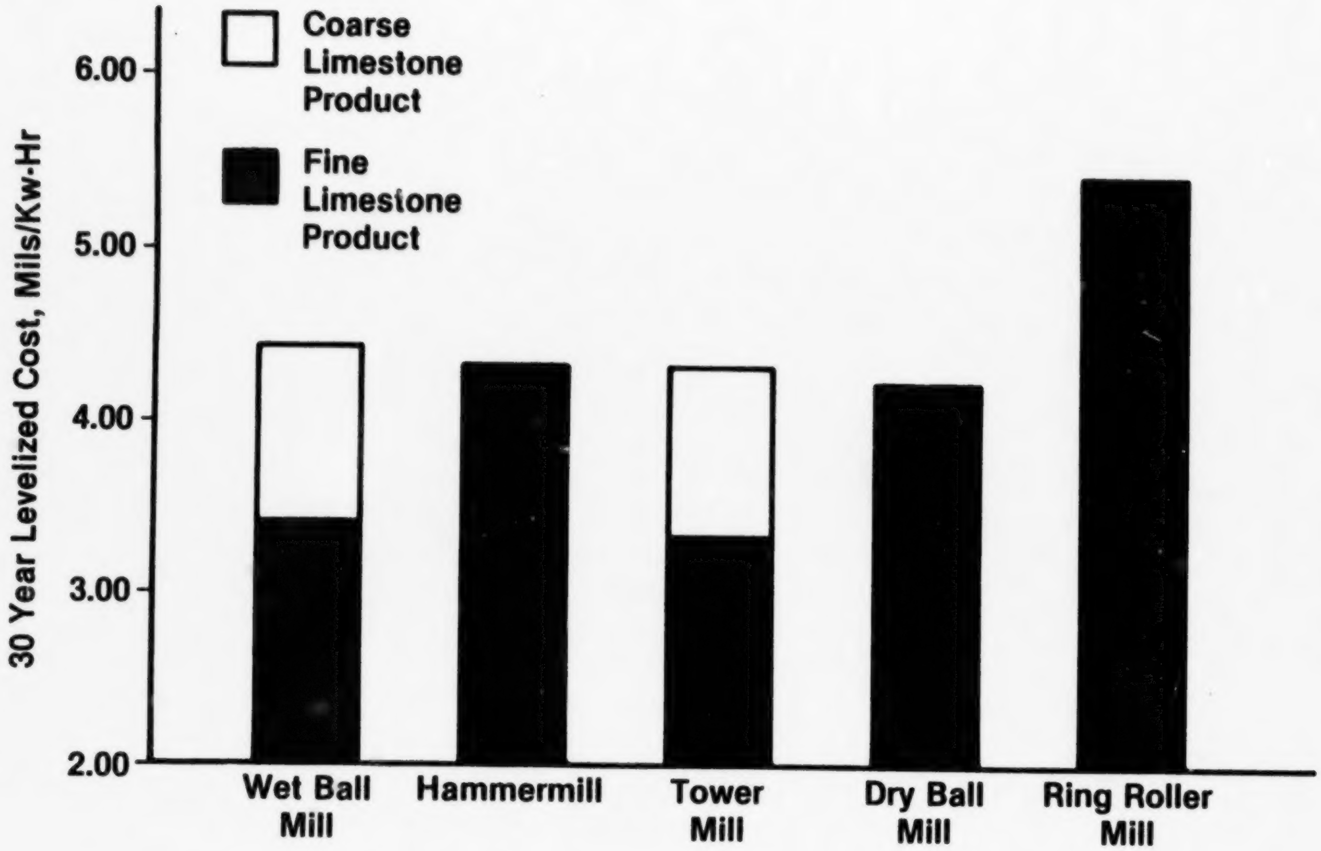


FIG. 3. LEVELIZED COSTS OF LIMESTONE REAGENT PREPARATION FACILITIES FOR HIGH SULFUR, 500MW PLANT

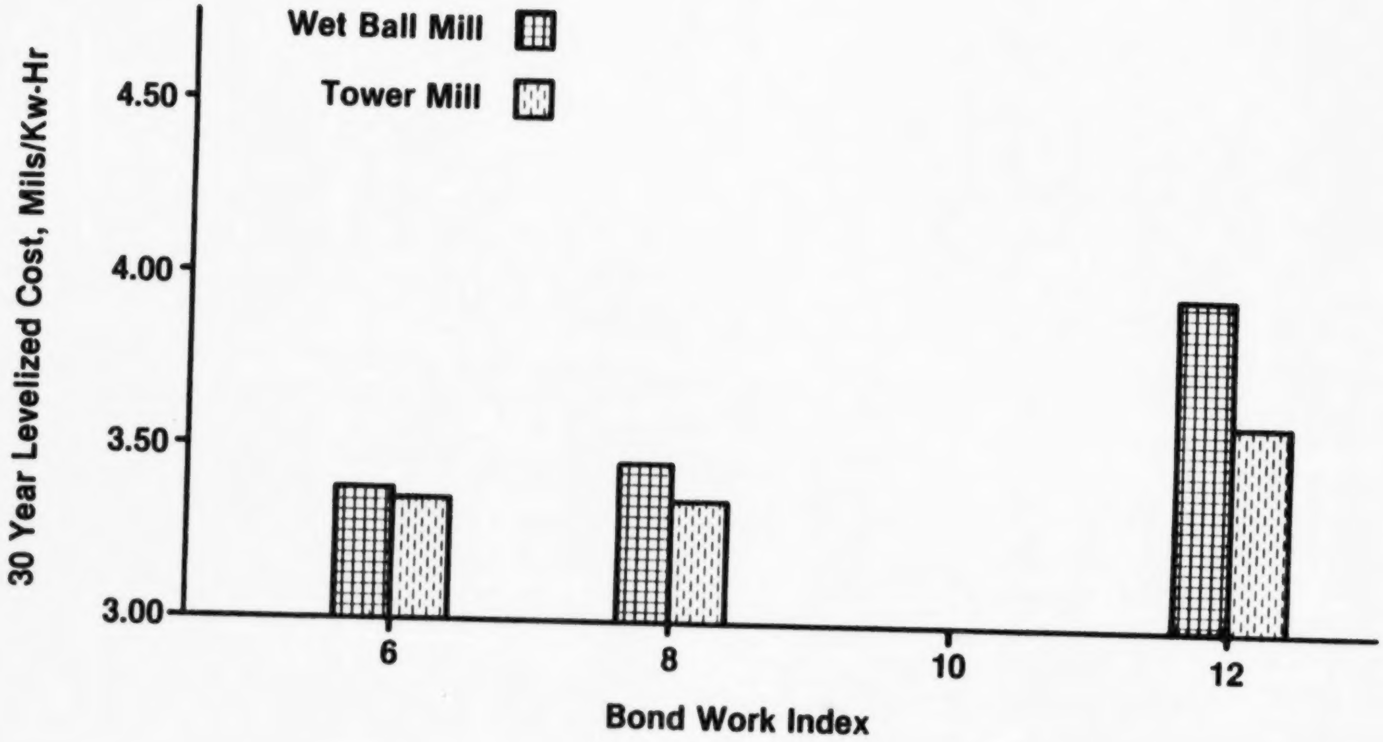


FIG. 4. EFFECT OF LIMESTONE HARDNESS ON REAGENT PREPARATION FACILITY COSTS

LIMESTONE SELECTION TESTING

Following the original EPRI testing of the ball mill grinding circuit at CILCo's Duck Creek station, the utility planned a study of alternate sources of limestone with the objective of selecting the most economical long-term supply of reagent. The utility allowed EPRI to participate in the study for the purpose of comparing laboratory evaluation of the limestones to the commercial tests to determine if laboratory data can be used to predict full-scale performance.

Three limestones were tested and compared to the limestone being used at the plant (Columbia). The properties of these limestones are given in Table 4. The limestone designations in Table 4 refer to the following sources:

Adams:	Adams Stone & Material, Inc., Quincy, IL.
Central:	Central Stone Co., Huntington, MO.
Linwood:	Linwood Stone Producers Co., Buffalo, IA.
Columbia:	Columbia Quarry, Valmeyer, IL.

TABLE 4. PROPERTIES OF LIMESTONE USED IN SELECTION TESTS AT DUCK CREEK

Property	Adams	Central	Linwood	Columbia*
Geologic Formation	Burlington	Kimmswick	Cedar Valley	Kimmswick
Composition				
$CaCO_3$, wt%	94.0	98.0	94.4	97.0
$MgCO_3$, wt%	2.8	0.4	0.5	1.2
Inerts, wt%	2.6	1.1	4.1	1.8
Grindability Index	15.6	14.1	12.2	14.5

---

*Supply prior to test.

Previous test work at Duck Creek had shown that the Columbia stone gave much higher utilizations at a pH of ~5.8 when the grinding circuit produced a product of 90% -325 mesh (Figure 5). The limestone preparation system was altered such that this product size was produced using Columbia stone. All three of the test stones are of similar hardness (grindability) and were expected to give similar results. However, the Linwood stone produced a finer product at greater throughput than the other two stones (Table 5).

Laboratory reactivity tests at two pH levels indicated that at pH 5.5 (Figure 6) the three stones were about the same, with Linwood perhaps showing a slightly greater reactivity. At pH 6.0 (Figure 7), the Linwood had significantly higher reactivity. Tests at the Duck Creek station show in Figure 8 that the Linwood and Central stones are about the same at pH 5.6 with the Linwood being better utilized at higher pH values. Comparing the stones (Table 6) for 95% limestone utilization while maintaining 85% SO_2 removal shows only the Adams stone to require greater dibasic acid (DBA) concentrations to maintain the desired SO_2 removal. The laboratory tests depicted the behavior of the Linwood and Central stones fairly accurately, but the behavior of the Adams stone could not be predicted from the laboratory reactivity test.

TABLE 5. EFFECT OF LIMESTONE FEED RATE ON PRODUCT PARTICLE SIZE AND GRINDING ENERGY

Limestone	Mill Feed % -200 mesh	Product Size, % -325 mesh	Grinding Energy, kWhr/ton
Adams	20	95	32.8
	25	91	26.2
Central	25	95	26.2
	30	95	21.9
	34	91	19.3
Linwood	27	97	24.3
	33	94	19.9
	38	96	17.3

TABLE 6. OPERATING CONDITIONS TO ACHIEVE 95% LIMESTONE UTILIZATION AND 85% SO_2 REMOVAL

Limestone	pH	DBA Conc., ppm
Adams	5.3	400
Central	5.6	200
Linwood	5.6	200
Columbia	5.6	200

Using the above data, the cost of each limestone was calculated assuming the following conditions:

Plant Capacity	0.65
Coal Sulfur Content	3.2%
SO_2 Absorption Rate	4.0 lb-mol/min
Limestone Utilization	95%
SO_2 Removal	85%

Annual reagent costs are given in Table 7.

TABLE 7. ANNUAL REAGENT COST FOR DIFFERENT LIMESTONES AT DUCK CREEK

Limestone	Delivered Cost, $ton	Quantity tons/yr	Cost, $1000/yr	DBA Cost, $1000/yr	Total Annual Cost $1000/yr
Adams	11.24	118,000	1,330	180	1,510
Central	13.20	113,000	1,490	90	1,580
Linwood	15.89	117,000	1,860	90	1,950
Columbia	14.07	114,000	1,600	90	1,690

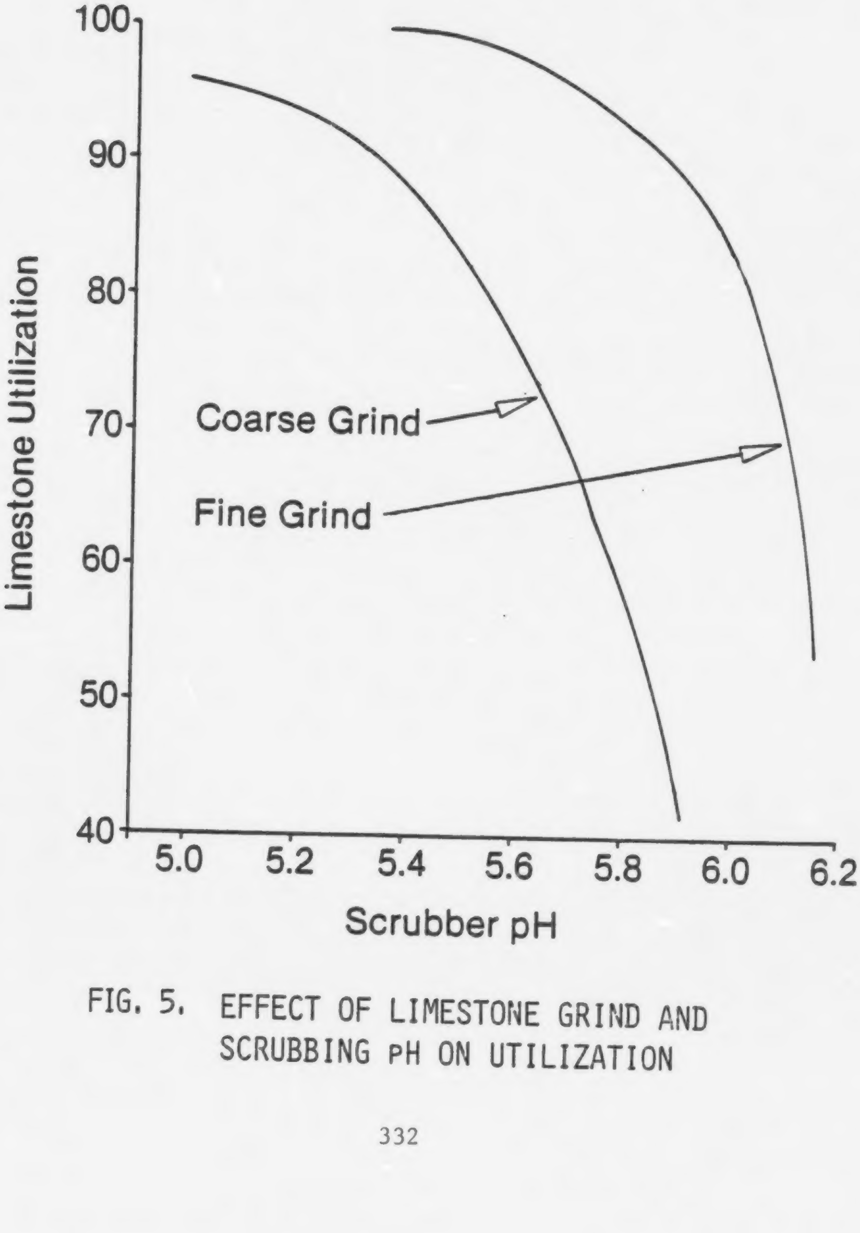


FIG. 5. EFFECT OF LIMESTONE GRIND AND SCRUBBING pH ON UTILIZATION

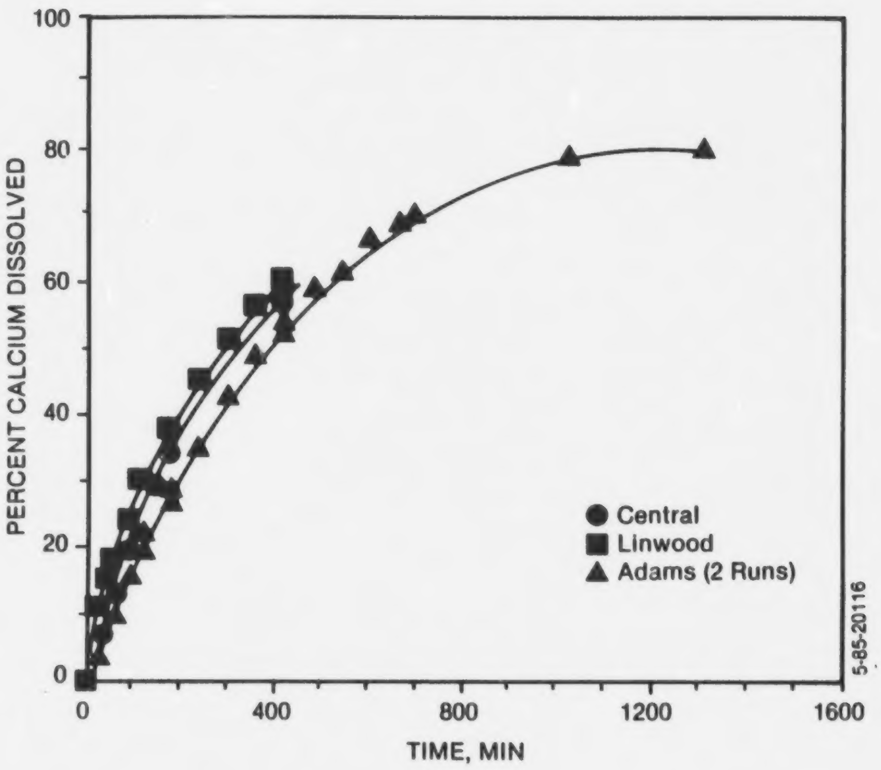


FIG. 6. RATE OF SOLUTION OF LIMESTONE AT pH 5.5

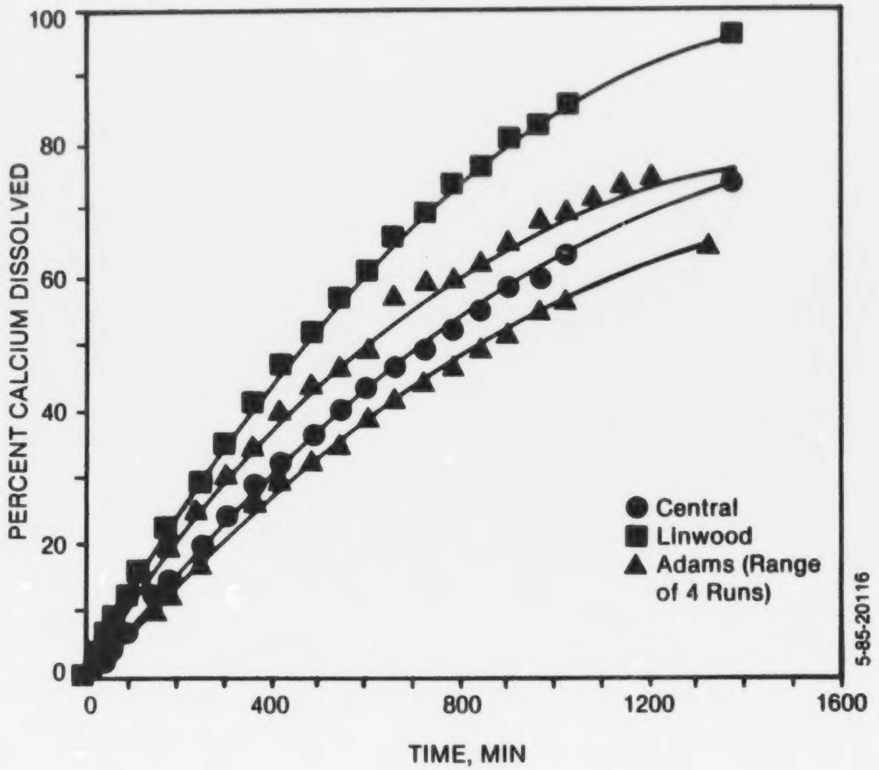


FIG. 7. RATE OF SOLUTION OF LIMESTONE AT pH 6.0

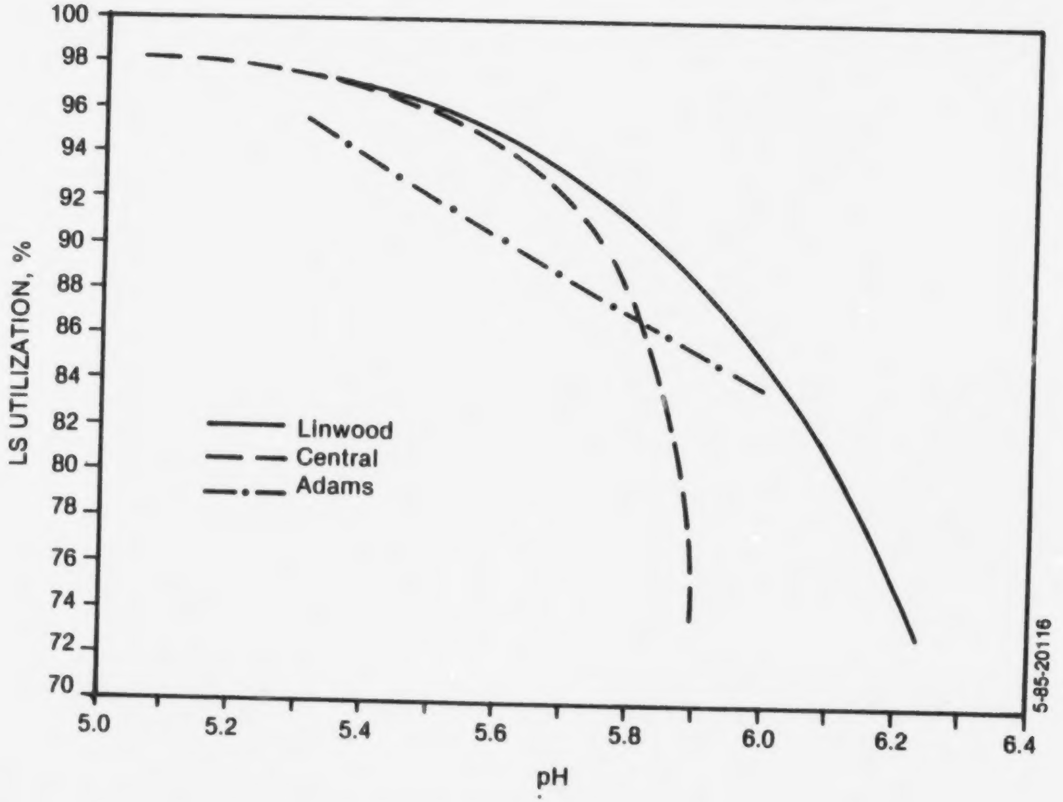


FIG. 8. EFFECT OF pH ON LIMESTONE UTILIZATION AT DUCK CREEK

All of these limestones are of sufficient quality to achieve the desired results, and costs indicate that the Adams and Central stones would be less expensive than the Columbia stone.

CONCLUSIONS

- The major factors affecting dissolution rate of limestone in FGD systems are the pH of scrubber liquor and the particle size distribution of the limestone.

- A tower mill and wet ball mill are the mills of greater energy efficiency for grinding limestone.

- Estimated costs for a limestone reagent preparation system show that the two systems of lowest cost are those using a tower mill and a closed circuit wet ball mill.

- The cost of a system to grind limestone to 90% less than 325 mesh is less than that to grind to 80% less than 200 mesh because of the decreased reagent required when using a finely ground stone.

- The cost of a grinding system increases with increasing hardness of the limestone.

- The limestone reactivity test developed by Radian for EPRI does not predict the behavior of all limestones in full-scale equipment.

- Two of the three limestones tested at the Duck Creek station of CILCo would be a less expensive source of limestone for the FGD system reagent.

RECOMMENDATIONS

- Further development work on the limestone reactivity test should be completed and the test results compared to full-scale testing of limestones.

- Comparisons of the tower mill and wet ball mill should be made at full-scale to confirm the efficiency of the tower mill.

Session 5: MATERIALS OF CONSTRUCTION

Charles E. Dene, Chairman
Electric Power Research Institute
Palo Alto, CA

FAILURE ANALYSIS
OF FGD SYSTEM COMPONENTS

Gary D. Jones
Radian Corporation
Research Triangle Park, NC

Peter F. Ellis II
Dennis M. Anliker
Radian Corporation
Austin, TX

Dorothy A. Stewart
Electric Power Research Institute
Palo Alto, CA

ABSTRACT

As part of a program sponsored by the Electric Power Research Institute (EPRI), Radian has analyzed equipment failures at several flue gas desulfurization (FGD) system installations. Both metallic and non-metallic material failures were encountered. Failures of non-metallic components include a variety of organic coatings applied to vessel walls and rubber linings applied to vessel walls and pump impellers. The metallic failures include air sparger anchors, nozzles, a limestone storage tank and an agitator shaft. While in some cases the failure was associated with installation, in most cases the failure was attributed to inappropriate materials or improper process operation. In each instance, the most probable cause of failure was determined and recommendations made to alleviate future occurrences. Several of the analyses and solutions are applicable to other systems where similar problems have occurred. The results illustrate how failure analysis of chronic problems can reduce the maintenance requirements of the FGD system.

INTRODUCTION

Flue gas desulfurization (FGD) systems have been used for many years and many of the early problems with these systems have been solved. However, difficulties still remain with regard to both process chemistry and materials. For example, corrosion, or unexpected degradation, of materials has reduced the FGD system reliability and availability. Such problems are often difficult to solve since only the symptom may be apparent, and the real cause obscured. This paper describes the results of a project aimed at defining and solving several specific materials problems that will interest FGD operators.

This project is sponsored by the Electric Power Research Institute (RP2248-2). Since September 1982, Radian Corporation has performed FGD failure analyses at several utilities. This paper presents the background and results of several failure investigations and also some of the general conclusions that can be drawn by examining the collective results.

A variety of failures have been investigated involving an equal variety of FGD system components. For purposes of presentation, these are separated into two categories, non-metallic materials and metallic materials. Non-metallic material failures are considered first and this section discusses the performance of organic coatings and rubber linings. Next, the section on metallic materials considers several failures involving component fractures and accelerated wear by corrosion and erosion. Conclusions are presented separately in each of the two sections.

FAILURE OF NON-METALLIC MATERIALS

The non-metallic failures investigated fall into two general categories. The first involves organic coatings applied over a carbon steel substrate. Typically, these are thin coatings that are applied by spray or by trowel to the substrate. They sometimes contain a filler. Probably the most common is a polyester resin combined with a flaked glass filler. These coatings are common in FGD systems in a variety of locations including absorbers, tanks and ducts. They are popular because of their relatively low cost and ease of application. Two of the failure investigations involved polyester coatings with fillers.

The second type of non-metallic failures encountered involved rubber linings applied over a metallic substrate. Their purpose is the same as that of the organic coatings, to protect the substrate from attack. The material in this case is often natural gum rubber. In absorbers rubber is used in sheet form and applied in panels over the substrate. In other types of applications, for example, pump impellers, rubber is usually cast-applied. Three of the failure investigations involved rubber linings.

CASE HISTORIES

Failure of a Flaked Glass Polyester Coating in an Absorber

Minnesota Power's Milton R. Young Station has experienced severe blistering of the interior coating of the absorber/recycle tank. Figure 1 shows a detail of the tank wall where the blisters appear as lighter areas. Some of the blisters had burst, exposing the substrate to corrosive attack. An example is shown in Figure 2. The blisters occurred throughout the lower portion of the vessel but were concentrated at the apparent liquid level. The original coating was six years old with some patched areas. During initial operation of the FGD system, the liquid level has varied widely due to an ineffective level control scheme which has subsequently been replaced.

Analysis of the failed material indicated that it was correct for the specification and had been properly cured. Porosity was normal and there was no evidence of chemical attack. Thickness was acceptable and the distribution of glass flakes was good. Elemental analysis indicated iron on both sides of the coating; other components were as expected (1).

The material exhibited signs of the classic failure mechanism initiated by diffusion of water, gases and corrosive ions through the coating (2). This type of failure is often encountered in situations where the material is alternately wet and dry. Thus, the failure may have been accelerated by erratic level control during the initial phases of system operation. In addition, plant personnel indicated that the coating received little or no inspection and maintenance during the first several years. It was concluded that this material failed as a result of being past its useful life in this service. Good level control and an inspection/maintenance program in place from start-up might have extended its service life to some extent.

Coating Failures in an Outlet Duct

Soon after start-up, Texas Utilities' Martin Lake Station experienced failure of the flaked glass polyester coating in the outlet ducts of their FGD systems. The failures were restricted to the downcomer zones located on the duct wall where cool, moist treated flue gas encountered hot, by-passed flue gas in the outlet/bypass duct. The outlet/bypass duct is illustrated in Figure 3. The original coating, Cellcoat 282X, had experienced rapid and severe failure in the downcomer zones of the outlet. In areas not under the downcomers the original coating was in good condition. The downcomer area experiences wet/dry conditions and the whole outlet duct is subject to very large temperature excursions during start-up and upset conditions. During these periods, the temperature can get as high as 350 to 450 degrees F (3). The combination of wet/dry conditions and by-passed flue gas can create locally high concentrations of sulfurous and sulfuric acid on the surface (4) contributing to prompt coating failure.

Reproduced from best available copy.

Figure 1. View of the interior wall of a slurry recycle tank at Milton R. Young Station. The liquid line is indicated by the arrows. The lighter patches indicate blisters. The unblistered areas below the liquid line were reddish from rust bleed-through.

Figure 2. View of a recycle tank wall blister which had ruptured, exposing the substrate to corrosive slurry. As a result, severe corrosion of the carbon steel substrate had occurred. The diameter of thin blister was about four inches.

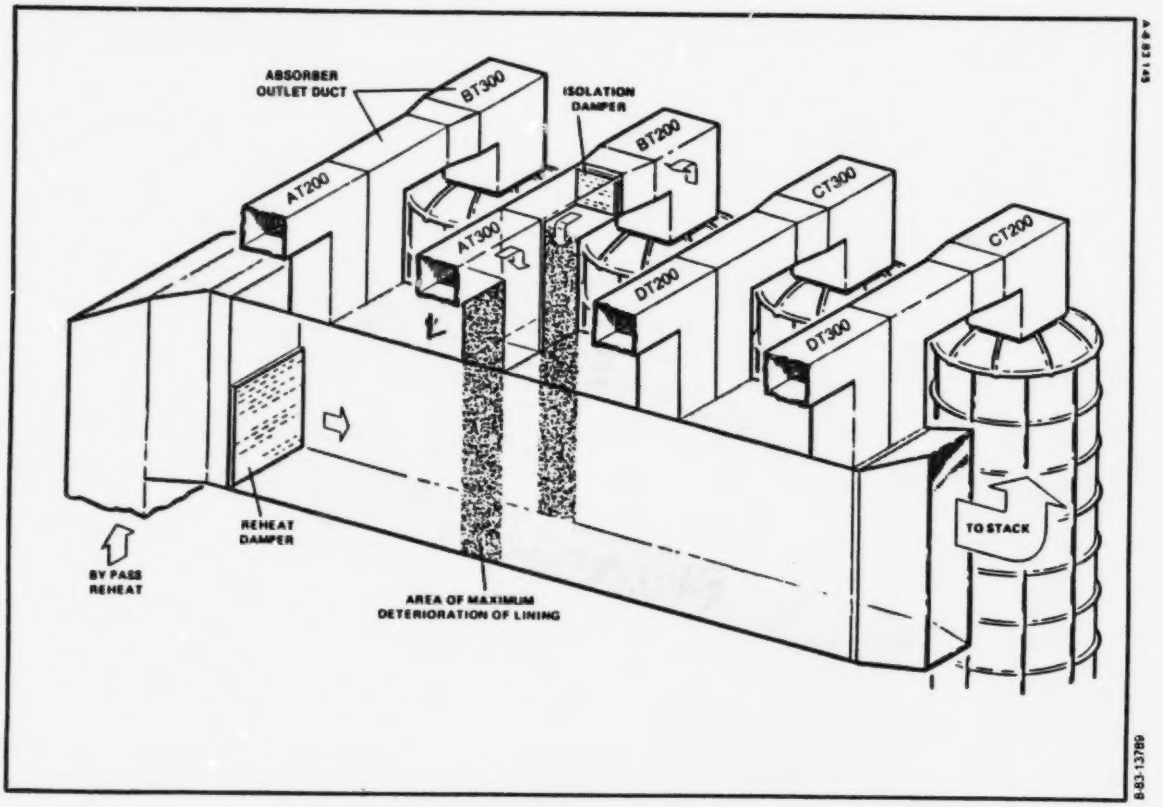

ABSORBER OUTLET DUCT
BT300
ISOLATION DAMPER
BT200
AT200
AT300
CT300
DT200
CT200
DT300
REHEAT DAMPER
BY PASS REHEAT
TO STACK
AREA OF MAXIMUM DETERIORATION OF LINING
A-493-145
8-83-13789

Figure 3. Bypass/Outlet Duct at Martin Lake Unit 2. All three units are essentially identical. Though zones of maximum deterioration are shown for only two absorber outlets, all eight have similar attack. These zones of maximum deterioration are designated "downcomer zones".

The material in several downcomer zones had been replaced with a variety of materials for testing purposes. Many of these had failed as well. A list of the coatings tested in the Unit 2 downcomers is presented in Table 1. Other materials were tested at Martin Lake in other outlet ducts; however, these units were operating and therefore not available for inspection at the time of this investigation.

Selected portions of the duct wall were removed and analyzed by Radian. These analyses revealed that the application of original 282X was good and that the material between downcomers showed no sign of failure. However, the 282X in the downcomer zone showed signs of cohesive failure. This specimen had been in downcomer service for only one month (one start-up/shut-down cycle). Cellcoat 871X, also in downcomer service, was performing better than the other test materials. The other materials examined by Radian did not appear to be suitable for this application. These included Flakeline 103, Martek Duromar 400 and Con/Chem Fiber/Crete.

The high temperatures, large thermal excursions and presence of wet/dry conditions combined to cause cohesive and adhesive failure of several of the coatings. One had become so friable that the coating was removed during brush blasting. The combination that seemed to work best was the Cellcoat 871X, which consists of a glass flake filled vinylester undercoat with a flouroelastomer topcoat. Reportedly, other flouroelastomers also performed well in this service, pointing out the importance of a vapor barrier when wet/dry conditions are present.

Degradation of a Rubber Lining in a Absorber, Case 1

One failure of a rubber lining in an absorber occurred at Colorado Ute's Craig Station. Portions of the rubber lining in the absorber were degrading rapidly while other areas were like new. The rubber was Gates 1375 and about three years old. The failed areas had low durometer values and failure was limited to whole sheets. The failed sheets were located in various areas in the absorber rather than in a localized area. An example is shown in Figure 4 where a panel of degraded rubber is next to a panel that is in good condition. This photograph was taken in the cone section of the absorber. As shown in Figure 5, the degraded rubber has significantly lower durometer reading.

Combustion and elemental analyses of both the good and failed material were performed. The results indicated that the failed rubber had a different composition than the good rubber. Specifically, the failed rubber had a higher H:C ratio and different concentrations of inorganic fillers. Comparison of the results also showed that the failed rubber was of different composition than the good rubber. It had less carbon black filler than the good rubber and was also much lower in silica flour filler. Silica flour is added to rubber to impart hardness and chemical resistance. Further, its reduced phosphorus level may have affected the rubbers's chemical resistance. The failed rubber had properties unsuitable for this service. It is also clear that this failure was not due to application (5). This failure points up the need for a more definitive and measurable specification for rubber materials used in FGD service.

Table 1

INSPECTION RESULTS FOR TRIAL COATINGS APPLIED TO OUTLET/BYPASS DOWNCOMMER ZONES IN MARTIN LAKE STEAM ELECTRIC STATION'S UNIT 2

Material Sample Number	Location/Service History	Appearance*
Flakeline 282X (Sample 8)	From duct wall between BT200 and BT300 downcomer zones. In service since 5/78.	Not inspected during visit. Material on sample panel was sound.
Flakeline 282X (Sample 5)	From near ceiling height in downcomer zone of tower DT200. This tower had been in service for about one month prior to inspection, so the sample had about 5 years dry service followed by one month downcomer zone service.	Good appearance (laboratory examination showed incipient failure).
Ceilcote 871X (Sample 6)	From ceiling height of BT300 downcomer. In service since 6/81.	Good appearance. One area of failure on sidewall. Appears to be at edge of 871X layer.
Flakeline 103 (Sample 7)	From ceiling height in BT300 downcomer. In service since 7/82.	Not inspected. Scaffold not in position.
Martek Duromar 400	Located in AT300 downcomer. Installed 7/82.	Failed: The coating was covered with friable blisters about 0.5-1.0 inch in diameter. Brush blasting after inspection removed the Martek Duromar 4000 and no sample was sent to Radian.
Con/chem Fibre/crete (Sample 4)	Located as patches in BT200 downcomer. Installed 7/82.	Failed: Vertical weld visible through sample/inspection area. Lining appears fair to one side of seam, but has large (>6 inches) blisters on other side. Also horizontal line of blackened blisters.

---

*Observation qualified because the downcomer surfaces were coated with 0.5-1.0 inch of flyash deposition, masking the surface.

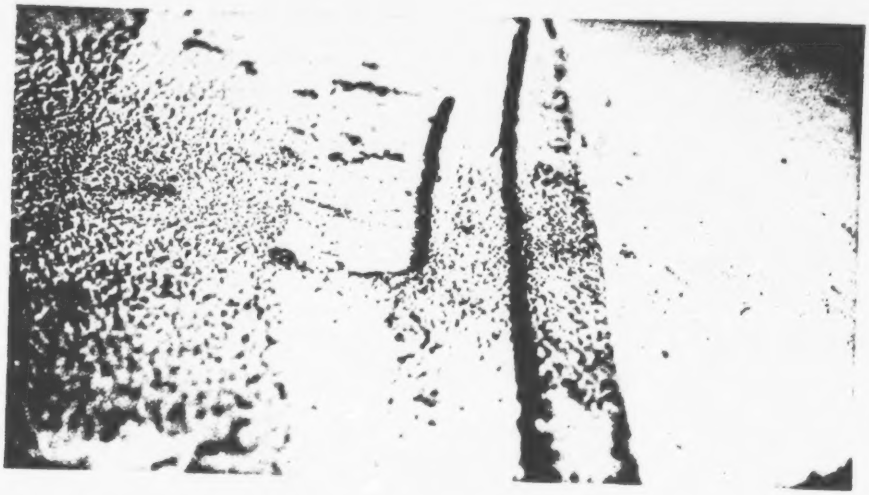


Figure 4. Panel of soft, bad rubber at left next to a panel of good rubber at the right on the cone of Module 1C at Craig Station. Note the crusted appearance of the bad scrubber which has had a rectangular sample removed. This photo also shows that where the bad rubber overlaps the good at the seam, it is degraded to the same extent as the rest of the bad sheet.

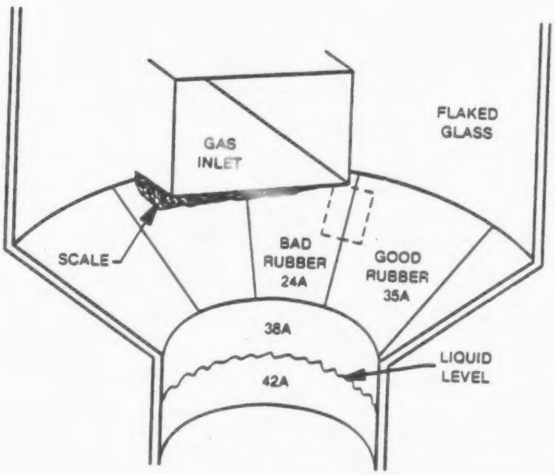

GAS
INLET
FLAKED
GLASS
SCALE
BAD
RUBBER
24A
GOOD
RUBBER
35A
38A
42A
LIQUID
LEVEL
70A3285

Figure 5. Averaged durometer readings on panels of rubber on the dip leg of Module 1C. Values shown are shown Shore A hardness scale. Dotted box indicates area of photograph in Figure 4.

Degradation of Rubber Lining in an Absorber, Case 2

A second failure of rubber lining in an absorber was investigated at Monongahela Power Company's Pleasants Station. The original material, Goodyear LS61 natural gum rubber, had experienced severe blistering and had been replaced with chlorobutyl rubber. A drawing showing the materials used in the scrubber and recirculation tank is shown in Figure 6. One of the chlorobutyl rubbers, Goodyear LS582, had operated for two years without problems. A second chlorobutyl, calendered B.F. Goodrich 1055, had failed by severe blistering upon curing. A third chlorobutyl, extruded BFG 1055, was used to replace the calendered material. The two BFG 1055's were purportedly the same material except that the calendered material consisted of numerous thin sheets pressed together during manufacture to form a 0.25 inch sheet and the extruded material was produced as a single 0.25 inch sheet.

Pleasants Station personnel had tested several rubbers as test panels in an apparatus resembling a large "Atlas cell" through which absorber slurry circulated. These tests showed that the Goodyear 561 would blister whether fully or partially cured. Another natural gum rubber also blistered. However, no blistering occurred on panels installed with external thermal insulation, indicating the existence of a "cold wall" effect. Good results were obtained by two extruded chlorobutyl rubbers, BFG 1055 and Goodyear LS582, and one tri-laminate, Goodyear 531 20-200 Triflex. The results are summarized in Table 2.

Examination of the failed calendered chlorobutyl rubber indicated that adhesive failure occurred in the tie-gum especially in the seam overlap areas. In other areas there was poor adhesion with the substrate behind blisters. Composition and hardness were typical for a chlorobutyl rubber. The calendered material also showed considerable porosity at the laminae interface.

While there was no representative sample of the natural gum rubber available for analysis, it was deduced that it had failed as a result of the the "cold wall" effect. In this failure mechanism, water diffuses into voids and resulting corrosion products at the rubber-steel interface creating an osmotic pressure that cause blisters to form and grow. This conclusion is supported by the fact that rubber linings on the scrubber internals, e.g. dip legs, did not experience blistering. The calendered chlorobutyl failed due to poor application; the seam tapers were much too narrow tending to trap liquid solvent, and contact with the substrate was poor in some areas (6).

Failure of Rubber Linings of Pump Impellers

In a different application of rubber materials, West Penn Power's Mitchell Station experienced rapid failure of several of their pump impellers. These impellers consisted of a carbon steel core encapsulated by a casting of natural gum rubber. Several pump impellers had lost significant amounts of rubber. Three affected pump impellers were received for analysis. These were from the thickener overflow pump, the thickener

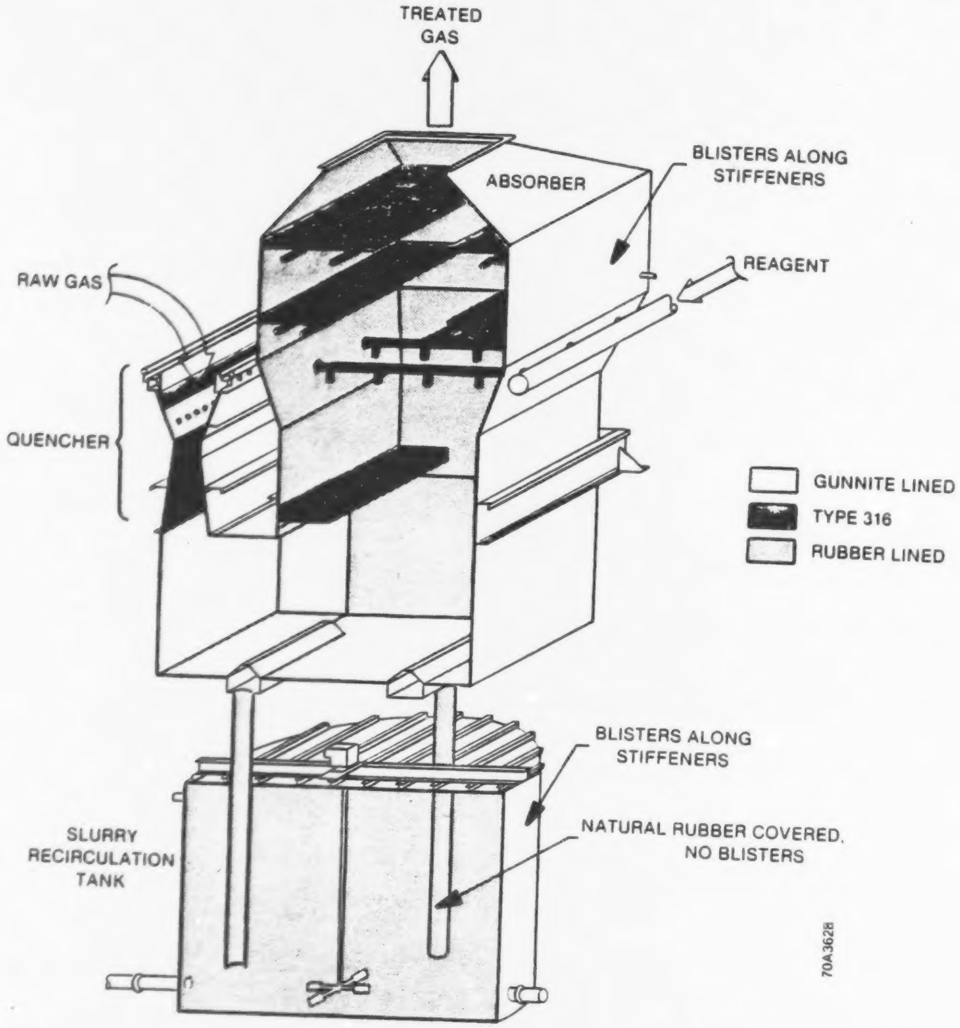

TREATED GAS
ABSORBER
BLISTERS ALONG STIFFENERS
RAW GAS
REAGENT
QUENCHER
GUNNITE LINED
TYPE 316
RUBBER LINED
BLISTERS ALONG STIFFENERS
SLURRY RECIRCULATION TANK
NATURAL RUBBER COVERED, NO BLISTERS
70A3628

Figure 6. Isometric drawing of an FGD system module at Pleasants Station.

Table 2

RESULTS OF RUBBER EVALUATION TESTS AT PLEASANTS STATION

Specimen	Cure	Visual Observations
Goodyear 561[1]	Undercured	Several blisters, more concentrated in the liquid area.
Goodyear 561[1]	Fully cured	Smaller blisters, same number and density.
B. F. Goodrich 1032[1]	Fully cured	Blistered.
Goodyear 531[2] 20-200 Triflex	Fully cured	Good overall appearance. Some small holes.
B. F. Goodrich 1008[3]	Fully cured	Cracked in vapor zone. Appearance of cracks similar to ozone cracking.
B. F. Goodrich 1055[4]	Fully cured	Good appearance.
Goodyear LS 582[4]	Fully cured	Good appearance.

---

[1] Natural gum rubber.

[2] A tri-laminate: chlorobutyl rubber (outer) - hard rubber (middle) - natural rubber (inner)

[3] A tri-laminate: natural rubber - hard rubber - natural rubber.

[4] Extruded chlorobutyl rubber.

Source: Unpublished data provided by Pleasants Station personnel.

underflow pump and the centrate return pump. Other pumps had experienced similar problems. Descriptions of the pump impellers analyzed are contained in Table 3.

The thickener overflow pump showed signs of poor adhesion and, in particular, a large void on the rim of the impeller between the steel and the rubber. All of the rubbers showed composition and hardness typical for natural gum rubber, 45 to 55 Shore A hardness. An analysis of the pump speeds, however, showed that the pumps were operated at overspeed conditions. This was due to the fact that the pumps were working against larger heads than were anticipated in the design. The result was an actual tip speed that was about 13% greater than recommended for rubber with this hardness range, resulting in an overstress of about 25 to 50 percent at the impeller rims.

It was concluded that the thickener overflow impeller failed because overspeed operation imparted excessive forces on the rubber. The failure originated at a void between the steel and rubber, but it appears that overspeed operation would have eventually caused failure even in the absence of the defect. The initial cause of failure on the other pumps is unknown, but secondary damage was due to high centrifugal forces caused by overspeed operation (7).

CONCLUSIONS REGARDING NON-METALLIC MATERIALS

While it is not possible to recommend a single approach or material that will work anywhere, the previous experiences and analysis do allow some conclusions to be drawn regarding coating/lining materials.

- The life of an organic coating is very application specific. A material that gives years of service in one application may give only a few months service in another environment. The worst environments appear to be those whose surface alternates between wet and dry. High temperatures, especially when experienced as sharp thermal cycles, can drastically shorten a coating's life.

- Where a wet/dry condition exists, the use of a material with a vapor barrier is advisable.

- The "cold wall" effect can contribute to failure, indicating that the lifetime of the coating or lining can be prolonged if the vessel is enclosed or insulated, or if the permeation resistance of the lining is increased.

- Independent industry standards are absent for the composition and formulation of rubber used in FGD systems. Such specifications and companion quality control procedures are needed. EPRI has a program underway that will address this need.

Table 3

DESCRIPTION OF THREE MITCHELL STATION PUMP IMPELLERS RECEIVED FOR FAILURE ANALYSIS

	Thickener Overflow	Thickener Underflow	Centrate Return
Manufacturer	Worthington	Ash	Warman
Model	5R142	A-6-6	3-2-C-AH
Function	Transfer low solids overflow from thickener overflow tank to absorber makeup and service water.	Transfer 35 percent solids underflow to sludge surge tanks.	Transfer centrate from centrate return tank to thickeners.
Service life (days)	419	Approximately 150	Approximately 150
Impeller			
Style	Closed (shrouded).	Closed (shrouded).	Open.
Support/Core	Steel web	Steel web	Solid steel core
Coating	Natural gum rubber	Natural gum rubber	Natural gum rubber
Outer diameter (in)	13.9	11.8	8.5*
Inner diameter (in)	6.0	4.1	1.3*
Width (in)	5.0	2.8	2.2*
Effective flow width (in)	2.6	2.2	1.9*
Number of vanes	3	3	5
Speed (rpm) (actual)	1480	1720	1660
Rim speed (ft/min)	5386	5313	Not calculated

---

*Dimensions of the steel core only.

- Without these specifications, it is difficult or impossible to properly select rubber materials. Also, without such standards, it is risky to allow "equivalent" materials to be substituted in lieu of proven materials, since the basis for "equivalency" is uncertain.

- It is very difficult, if not impossible, to prepare a metal surface in the field to the degree often specified by the coating/lining manufacturer. Therefore, it is important to have established quality control procedures in place during surface preparation and application of the coating/lining.

- While it is common to blame the application when a coating or lining fails, the findings of this EPRI study indicate that this is not a good assumption. In many cases, inappropriate materials selection or improper equipment operation were found to be the root cause of failure.

FAILURE OF METALLIC MATERIALS

The metallic failures investigated included an air sparger, an agitator shaft, a mix tank, spray nozzles and transfer piping. These cases can be divided into two types of failures, those involving a fracture and those involving some form of erosion. The air sparger and agitator shaft failures involved fractures, while erosion played a role in the failure of the other three.

CASE HISTORIES

Fracture of an Air Sparger Arm

This failure occurred at Texas Utilities Generating Company's Martin Lake Station. The failed component was an air sparger that was part of the FGD system's retrofitted forced oxidation system. Forced oxidation was achieved by introducing air into the reaction tank via a sparger array that consisted of a main header feeding six sparger arms. The air sparger is illustrated in Figure 7. Each arm was welded at the header and the extremity was anchored to a pedestal by a stainless steel U-bolt. In the failure investigated by EPRI, one of the sparger arms had broken at the weld and the U-bolt was fractured in two locations, as shown in the figure. The U-bolt was removed and analyzed. This mode of failure had occurred with other spargers in other absorbers. The sparger life was about three months.

The alloy was determined to be 317 stainless steel. Examination using the scanning electron microscope (SEM) revealed that the initial fracture, fracture B in the drawing, initiated in a thread root and was due to stress corrosion cracking (Figure 8). The second fracture, fracture A in the drawing, was due to rapid fatigue. The fact that only this fracture was scale free indicated that it had occurred after fracture B.

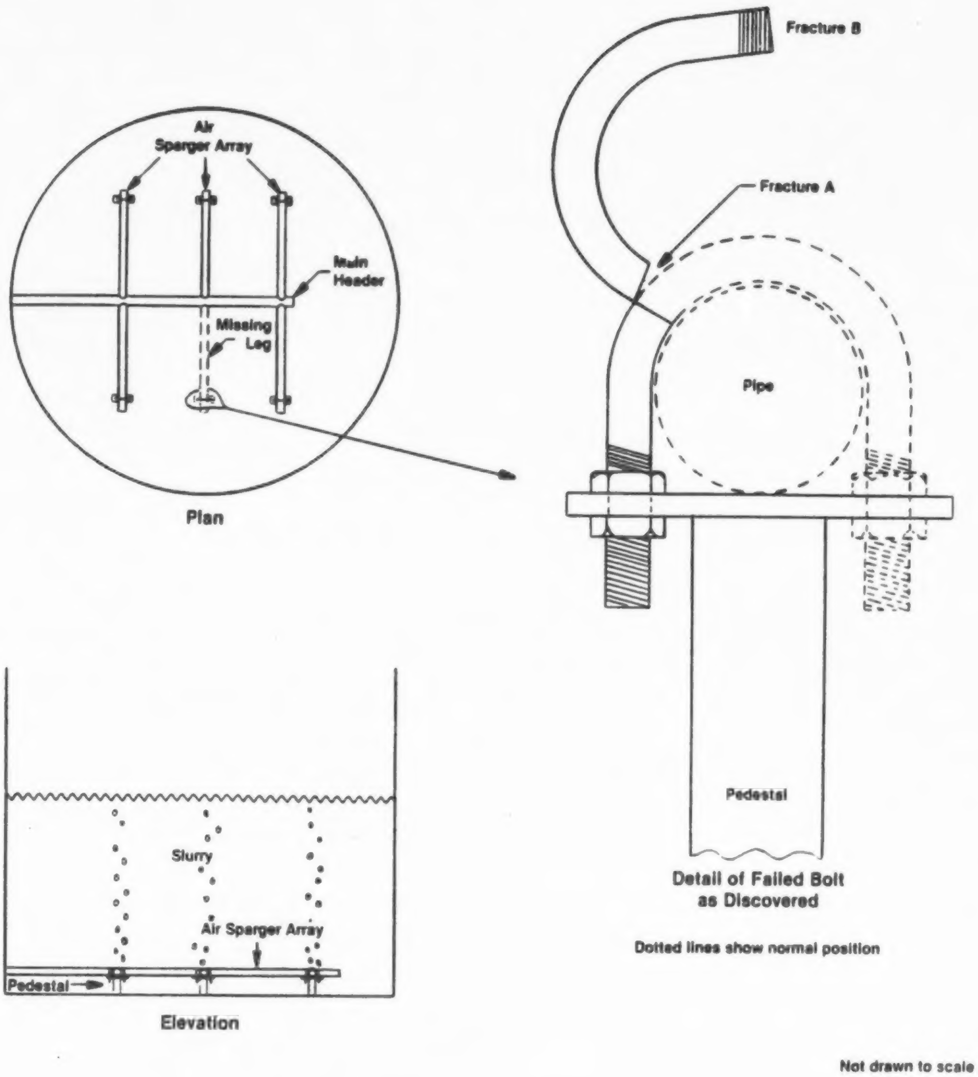

Air Sparger Array
Main Header
Missing Leg
Plan
Fracture B
Fracture A
Pipe
Pedestal
Detail of Failed Bolt as Discovered
Dotted lines show normal position
Slurry
Air Sparger Array
Pedestal
Elevation
Not drawn to scale

Figure 7. Plan, Elevation, and Detail Drawing of a Forced-Air Oxidation Sparger Array at Martin Lake Steam Generating Station.

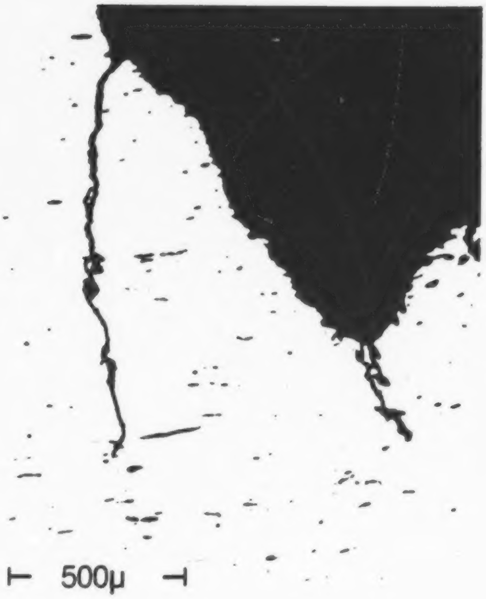


Figure 8 (left). Photomicrograph of a Longitudinal Cross Section of the U-bolt near Fracture B. The austenite grains are severely deformed from cold working in manufacture. Two branching, transgranular cracks are notable in this thread root.

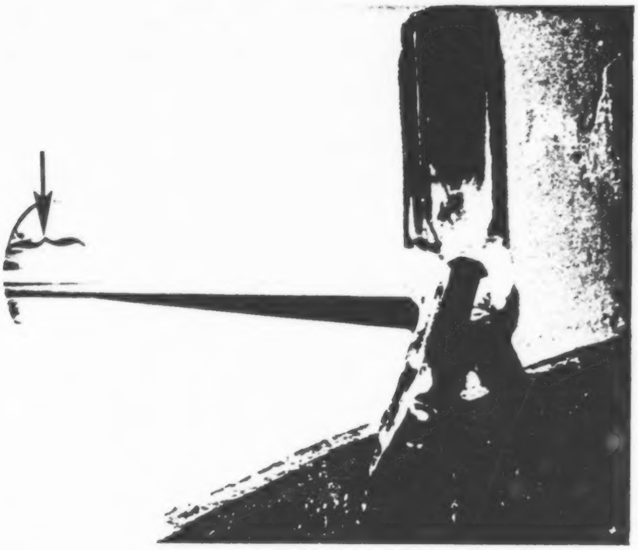


Figure 9. Agitator in the sump area of one of the towers at W.A. Parish Unit 8. This agitator is identical to the one which was the subject of investigation. The arrow indicates the approximate location of the shaft fracture.

The cause of the initial failure was stress corrosion cracking (SCC) in the thread areas aggravated by the presence of oxygen. This failure allowed the end of the arm to vibrate. The second failure of the U-bolt, and the weld failure, was due to this vibration. The SCC mechanism is accelerated by increasing concentrations of chloride and increasing concentrations of oxygen (8,9,10). As the plant closes its water balance, SCC of the 317 U-bolts is likely to become more frequent. The root cause of failure was inappropriate materials selection for this application. The problem can be corrected, relatively inexpensively, by replacing the U-bolts and nuts with an alternate alloy, for example, Hastelloy C-276.

Fracture of an Agitator Shaft

This failure occurred at Houston Lighting and Power's W.A. Parrish Station. The shaft of a slurry agitator was found to be broken after an upset outage. The agitator was located in the recirculation tank and was a side entry design. Figure 9 shows a functional agitator and the arrow shows the approximate location of the shaft fracture. The fracture was perpendicular to the shaft axis and had occurred after about 12 months of operation. A similar failure had previously occurred on another unit after 18 months of operation.

A portion of the shaft containing the fracture face was analyzed to determine the alloy and the type of metal fracture which had occurred. The alloy was 316L stainless steel and the tensile strength was typical for annealed 316L. The fracture face presented the classic signature of high-cycle rotating-bending fatigue with multiple origins. Type 316L has a low resistance to this form of attack.

High-cycle, low-stress, rotating-bending fatigue is a chronic process resulting from the application of a large number of low-amplitude stress cycles. It was not due to a sudden event. The failure was due to 316L being an inappropriate material for this application. This conclusion is further supported by the fact that West Penn Power's Mitchell station has a similar FGD system design, but uses rubber covered, carbon steel shafts which have experienced no failures in more than 2.5 years. In this case, a rubber-covered, high-strength, low-alloy steel would be a better material than 316L (11).

Localized Wear of Limestone Storage Tank Bottom

Colorado-Ute's Craig Station observed that a carbon steel limestone slurry storage tank was leaking. The tank, illustrated in Figure 10, was drained and inspected. The storage tank showed accelerated wear on its 0.25 inch thick carbon steel bottom. The wear was in the form of two concentric rings when the metal had been thinned, as shown in Figure 11. The vessel was agitated and contained a slurry of limestone ground to 90-95% through 400 mesh. Portions of the tank bottom were removed for analysis.

While the metal microstructure was normal for carbon steel, analysis by SEM disclosed evidence of electrochemical corrosion in all areas. In

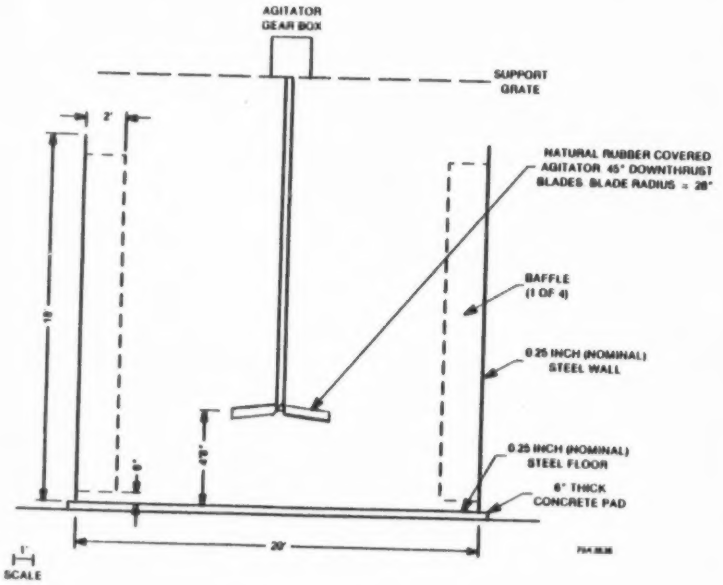

AGITATOR
GEAR BOX
SUPPORT
GRATE
2'
18'
NATURAL RUBBER COVERED
AGITATOR 45° DOWNTHRUST
BLADES BLADE RADIUS = 28"
BAFFLE
(1 OF 4)
0.25 INCH (NOMINAL)
STEEL WALL
48"
6"
0.25 INCH (NOMINAL)
STEEL FLOOR
6" THICK
CONCRETE PAD
20'
1'
SCALE

Figure 10 (left). Cross-Sectional Drawing of the Craig Unit 1 Limestone Slurry Storage Tank.

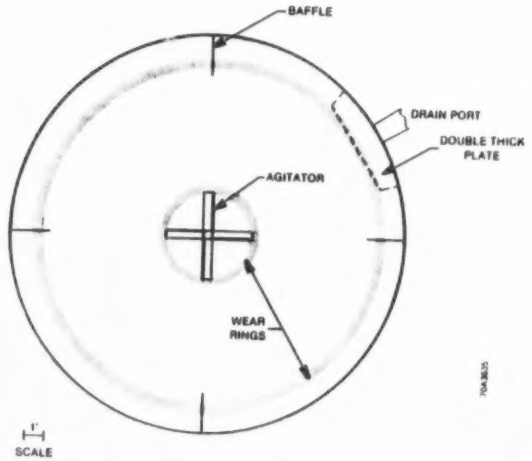

BAFFLE
DRAIN PORT
DOUBLE THICK
PLATE
AGITATOR
WEAR
RINGS
1'
SCALE

Figure 11 (left). Position of "wear rings", areas of excessive thinning and perforation, on floor of Craig Unit 1 limestone slurry storage tank.

addition, there were parallel grooves and some horseshoe pits on the surface of the worn area, indicating erosion. The metal loss was not due just to abrasion by the slurry particles, but due instead to the combined effects of erosion-corrosion. The wear rings coincide with areas where the direction of slurry flow changed sharply, creating greater turbulence. The increased turbulence and scouring action of the limestone slurry facilitated oxygen transport to the worn areas, thus increasing the rate of corrosion which is proportional to the rate of oxygen transfer to the surface. At the same time the slurry particles removed any protective oxide corrosion products exposing fresh metal to corrosive attack (12).

Rapid Wear of Absorber Spray Nozzles

At Arizona Public Service's Cholla Power Plant, stainless steel spray nozzles in the absorber were wearing out at two to six month intervals. The cost of replacement was estimated to be more than $120,000 per year plus labor for Unit 2. The nozzle received for analysis, shown in Figure 12, showed signs of tight cyclonic action. Most of the internals were worn away and the body had two perforations.

The FGD system operated with a coarse limestone grind, 59% through 325 mesh. Additional analysis of the limestone slurry indicated that one-third of the particles are siliceous. Furthermore, about half of the coarsest particles were siliceous. A photomicrograph in Figure 13 shows the typical absorber slurry and the presence of large, angular silicates.

The nozzle material was determined to be CF-8M, the cast equivalent of 316 stainless steel, and to have a hardness typical for this material. Analysis by SEM indicated no sign of corrosive metal loss. However, the surface was covered with angular markings indicating erosion.

It was concluded that the premature wear was due to severe and rapid erosion caused by the poor grind and high inerts content of the limestone. It has been shown that the erosion rate is proportional to the cube of the particle diameter. In this situation, there are two potential solutions. One is to use a limestone with a better grind and fewer inerts. This option would also benefit the limestone utilization efficiency. The second is to replace the nozzles with others made of either harder or more resilient material (13).

Excessive Erosion of a Limestone Slurry Pipeline

At the time of this investigation, Houston Lighting and Power's W.A. Parrish Station had experienced two failures of the pipeline that transferred limestone slurry from the ball mill to the reagent storage tank. The original pipeline between the ball mill and the reagent storage tank was schedule 40 carbon steel pipe which experienced rapid failure, especially at the elbows. At that time, the limestone grind was poor, 24% larger than 200 mesh. The grind was improved and the pipe replaced with schedule 80 carbon steel. This too experienced rapid failure. Both the limestone grind and sections of the Schedule 80 pipe were analyzed. A

Reproduced from
best available copy.

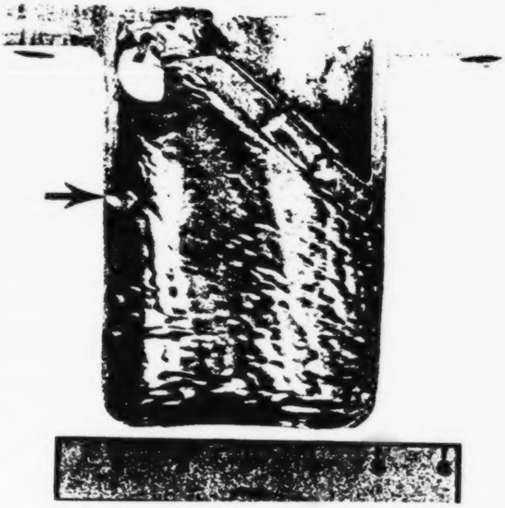


Figure 12. Interior surface of spray nozzle from Cholla Power Plant, Unit 2. Erosion-like flow marks are evident. The arrow indicates a small through wall perforation.

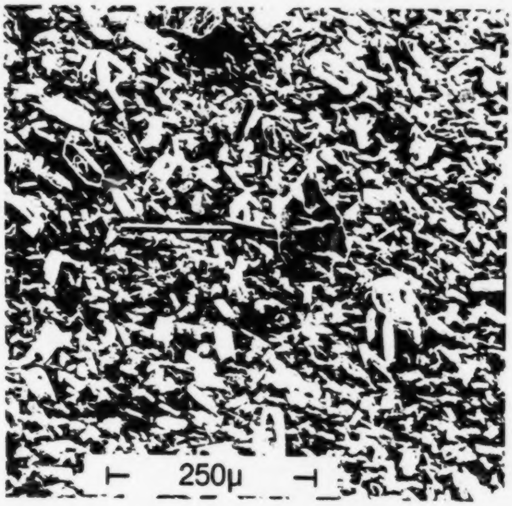


Figure 13. Scanning electron photomicrograph of a random sample of Unit 2 absorber slurry particles. Most particles are gypsum crystals smaller than 0.03 mm. The arrow indicates a large siliceous particle.

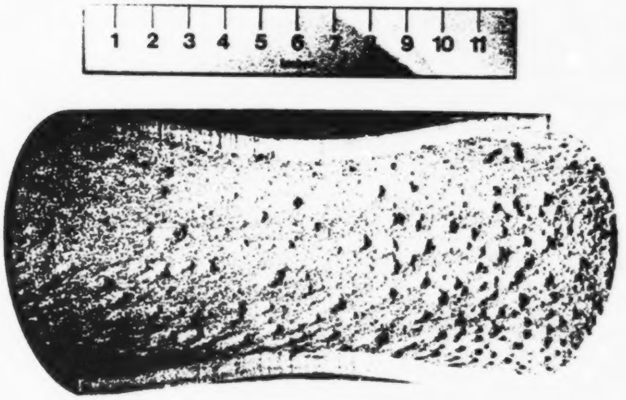


Figure 14. Internal surface of the extrodos of an elbow from W.A. Parish Unit 8 limestone slurry recycle line. The horseshoe shaped pits, characteristic of erosion-corrosion, were up to 75 mils deep.

view of the interior of one of the schedule 80 pipe specimens is shown in Figure 14.

The limestone grind was determined to be 84% less than 200 mesh and 76% less than 325 mesh, which is a fair-to-poor grind. Optical inspection of the interior surfaces of the schedule 80 pipe specimens indicated horseshoe pits 50 to 75 mils deep. The material was determined to be normal carbon steel with a normal microstructure and a normal hardness. SEM analysis showed the presence of smooth-bottom pits and square etch pits, visible at extreme magnification, indicating that electrochemical corrosion was taking place. The presence of horseshoe-shaped pits indicates that erosion was taking place as well.

Thus the failure was caused by an erosion-corrosion mechanism. Metal loss by corrosion is proportional to the rate of oxygen transfer to the metal surface. Erosion by the limestone slurry aids the process by removing the protective oxide layer, facilitating oxygen transport to the metal. Carbon steel is an unsuitable material for this service since it is susceptible to this type of attack. The solution was to replace the pipe with either rubber-lined pipe or a very hard material, such as cast basalt (14).

CONCLUSIONS REGARDING METALLIC MATERIALS

The experiences and resulting analyses described in the previous case histories allow several conclusions to be drawn regarding the use of metallic components in FGD systems.

- It is important to choose the correct alloy for each application and it is not possible to generalize that one material is always better than another. As shown in the failure of the agitator shaft, stainless steel was inferior to carbon steel in this application.

- What appears superficially to be simple erosion can often be the combined effects of corrosion and erosion.

- The combined effects of corrosion and erosion can cause rapid failure, especially when there is facilitated oxygen transport to the metal surface.

- Materials are not always at fault in a failure. Many times an improvement in process operations can improve a material's performance. For example, in two of the cases presented here, poor limestone grind contributed to the failure.

GENERAL OBSERVATIONS AND CONCLUSIONS

In addition to the conclusions specific to FGD system components, it is also possible to make some general conclusions about FGD system failures and their prevention.

Many FGD system components have lifetimes less than that of the FGD system itself. However, the actual life of any component can be affected by proper materials selection, and the existence or absence of adequate quality control, FGD system operation, and inspection/maintenance practices.

In many instances, the apparent cause of a failure is not the root cause and attempts to correct the problem without failure analysis will address the symptoms, but not the cause. This can result in recurring failures and, consequently, high maintenance costs.

The difference between a failure and a maintenance problem is often subtle and some corrosion failures frequently masquerade as mechanical or maintenance problems. In many cases a failure analysis of a recurring maintenance problem will suggest ways to eliminate the problem altogether. Two examples are given in this paper. In the case of the sparger arm and the case of the agitator shaft, the failure analysis team had been called to the plant to investigate another component but discovered the additional failure as part of the site inspections. In both cases the plant operators had not recognized the fractures as indicating a basic materials selection error likely to cause repeated outages. The cost of continued and repeated maintenance is often greater than the cost of correcting the materials problem, especially if the failure affects boiler operation or otherwise causes outages. The examples presented demonstrate the value of having trained failure analysis personnel present during normal maintenance outages of an FGD system, even if there are no pre-identified targets of investigation.

* * *

The work described in this paper was not funded by the U. S. Environmental Protection Agency, and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

REFERENCES

1. Aniiker, D.M., G.D. Jones and P.F. Ellis, Failure Analysis Report: SO_2 Absorber Coating, Milton R. Young Station, Minnkota Power Cooperative, Center, North Dakota, (Draft), Radian Corporation, 1983.

2. Berger, D.M., et al., "Evaluating Linings for Power Plant SO_2 Scrubbers," Power Engineering, November 1980, pp.71-75.

3. Ellis, P.F., *Failure Analysis Report*: *FGD System Bypass/Outlet Duct Linings, Martin Lake Steam Electric Station, Texas Utilities*, *Tatum, Texas*, (Draft), Radian Corporation, September 1984.

4. Burns & McDonnel, "Selective Condensate Test Report 82-129-3 and Supplement", prepared for Texas Utilities Generating Company, 1982.

5. Aniiker, D.M., P.F. Ellis and G.D. Jones, *Failure Analysis Report*: *SO_2 Absorber Lining, Craig Station, Colorado-Ute Electric Association, Craig, Colorado*, (Draft), Radian Corporation, May 1983.

6. Ellis, P.F., R.L. Nolen and G.D. Jones, *Failure Analysis Report*: *Chlorobutyl Rubber FGD Absorber Liners, Pleasant Station, Monongahela Power Company, Willow Creek, West Virginia*, (Draft), Radian Corporation, April 1984.

7. Ellis, P.F., R.L. Nolen and G.D. Jones, *Failure Analysis Report*: *FGD Slurry Dewatering Pump Impellers, Mitchell Station, West Penn Power, Monongahela, Pennsylvania*, (Draft), Radian Corporation, March 1984.

8. Ellis, P.F., and D.M. Aniiker, *Failure Analysis Report*: *FGD Forced-Air Oxidation Sparger Array, Martin Lake Steam Electric Station, Texas Utilities, Tatum, Texas*, (Draft), Radian Corporation, September 1983.

9. B.F. Brown, *Stress Corrosion Cracking Control Measures*, National Association of Corrosion Engineers (NACE), Houston, Texas, 1981.

10. Koch, G.H., J.A. Beavers, N.G. Thompson and W.E. Berry, *A Survey of the Performance of Candidate Construction Materials for Flue Gas Desulfurization Systems*, EPRI Project RP1871-1, Battelle-Columbus Laboratories, 1981.

11. Ellis, P.F., and K. Oberle, *Failure Analysis Report*: *Agitator Shaft from FGD Absorber Tower Reaction Tank, W.A. Parrish Plant, Unit 8, Houston Lighting and Power, Houston, Texas*, (Draft), Radian Corporation, February 1985.

12. Ellis, P.F., and D.M. Aniiker, *Failure Analysis Report*: *Limestone Slurry Storage Tank Bottom, Craig Station, Colorado-Ute Electric Association, Craig, Colorado*, (Draft), Radian Corporation, April, 1984.

13. D.M. Aniiker and P.F. Ellis, *Failure Analysis Report*: *FGD System Sprayer Nozzle, Cholla Power Plant, Arizona Public Service Company, Joseph City, Arizona*, (Draft), Radian Corporation, March 1984.

14. Ellis, P.F., and K. Oberle, *Failure Analysis Report*: *FGD Limestone Reagent Slurry Pipeline, W.A. Parrish Plant, Unit 8, Houston Lighting and Power, Houston, Texas*, (Draft), Radian Corporation, February 1985.

PERFORMANCE OF DUCT AND STACK MATERIALS IN WET FGD SYSTEMS

by: H. S. Rosenberg, G. H. Koch, C. W. Kistler, Jr.,
and J. A. Beavers
Battelle's Columbus Laboratories
Columbus, Ohio 43201

M. L. Meadows
Black & Veatch Engineers-Architects
Kansas City, Missouri 64114

D. A. Stewart
Electric Power Research Institute
Palo Alto, California 94303

ABSTRACT

In previous field surveys of construction materials for wet FGD systems on utility boilers, it was found that the major problem areas are outlet ducts and stacks. These components are critical in that a failure may result in complete loss of generating capacity for lengthy periods. Accordingly, EPRI is currently funding a study by Battelle on the causes of materials failures in FGD systems. As part of this study, Battelle analyzed the field performance of two outlet duct linings and three stack materials. The duct linings included a glass-flake-reinforced polyester at San Juan and an hydraulically bonded concrete at Gibson. The stack materials included a mica-flake-reinforced polyester lining at Duck Creek, an Alloy 625 flue at Bruce Mansfield, and an acid-resistant brick and mortar flue at Phillips. The latter two materials did not represent actual failures.

Field visits were made to each site by a team of specialists to (1) obtain background information, (2) inspect the duct or stack, and (3) collect samples of the materials for detailed analysis. The samples were analyzed by methods such as optical microscopy, scanning electron microscopy/energy dispersive X-ray spectroscopy, X-ray diffraction, and infrared spectroscopy. The results were used to evaluate the performance of the materials. The performance was found to depend upon the environmental conditions within the duct or stack. It appears that the most severe condition occurs when wet scrubbed gas is mixed with hot bypassed gas. Characterization of the environmental conditions is important in all cases in order to identify potential materials problems and develop solutions for them.

INTRODUCTION

A variety of construction materials have been used in the wet flue gas desulfurization (FGD) systems that have been built to date. These materials can be classified as follows:

- Metals
- Organic linings and plastics
- Ceramic and inorganic materials.

Metals ranging from carbon steel to nickel-base alloys, depending upon service conditions, have been used in most components of FGD systems. Organic linings have been used extensively in prescrubbers, absorbers, tanks, outlet ducts, and stacks. Inorganic linings have been used in prescrubbers, outlet ducts, and stacks.

In studies funded by the Electric Power Research Institute (EPRI), Battelle's Columbus Laboratories performed field surveys of construction materials for FGD systems (1,2). Information on materials performance was collected from wet FGD installations in operation, from major equipment suppliers for such systems, and from several A/E firms. Wherever possible, the data were collected by site visits, since this method generally yields the most complete and up-to-date information. To supplement the visits, information was also obtained by telephone discussions and correspondence exchange. In addition, contacts were made with several companies which manufacture materials with application in FGD systems.

It was found that the major materials problems are occurring with outlet ducts and stack linings. Outlet ducts and stacks are critical components in that failures may require complete boiler shutdown and loss of generating capacity for lengthy periods due to the lack of standby components or bypass capability. Because of the impact of materials failures on FGD system reliability, EPRI is currently funding a study by Battelle on the causes of these failures. This study involves site visits for field evaluations of the failures, laboratory analyses of samples collected in the field, and analysis of the data to establish the causes of the failures.

BACKGROUND

OUTLET DUCTS

Ducts are used to transport the flue gas in an FGD system. The outlet duct carries the flue gas from the absorber to the stack so that the interior surface is subjected to a variety of flue gas conditions depending upon the FGD system design. Because of the aggressive nature of these conditions, provisions must be made for protection against deterioration or corrosion. These provisions include the use of corrosion resistant alloys or nonmetallic linings and/or the use of flue gas reheat to minimize condensation.

Glass-flake-filled polyester and inert-flake-filled vinyl ester are the most commonly used types of organic linings in outlet ducts. Fluoroelastomer and epoxy linings have been used more recently at some installations. Inorganic linings are generally not used in wet environments, but their use in hot environments is growing because of temperature limitations with organic linings. A relatively new concept of using organic membranes below inorganic gunites has been developed. At least two gunite manufacturers now have installation specifications for use with membranes. Foamed borosilicate glass blocks have been installed in the outlet ducts of at least two FGD systems and represent full-scale field tests of this material. Alloys or alloy linings are not common, but Type 316L and Type 317L stainless steel and higher alloys such as Alloy 904L, Alloy 825, Alloy G, Alloy 625, and Alloy C-276 have been used in a few outlet ducts.

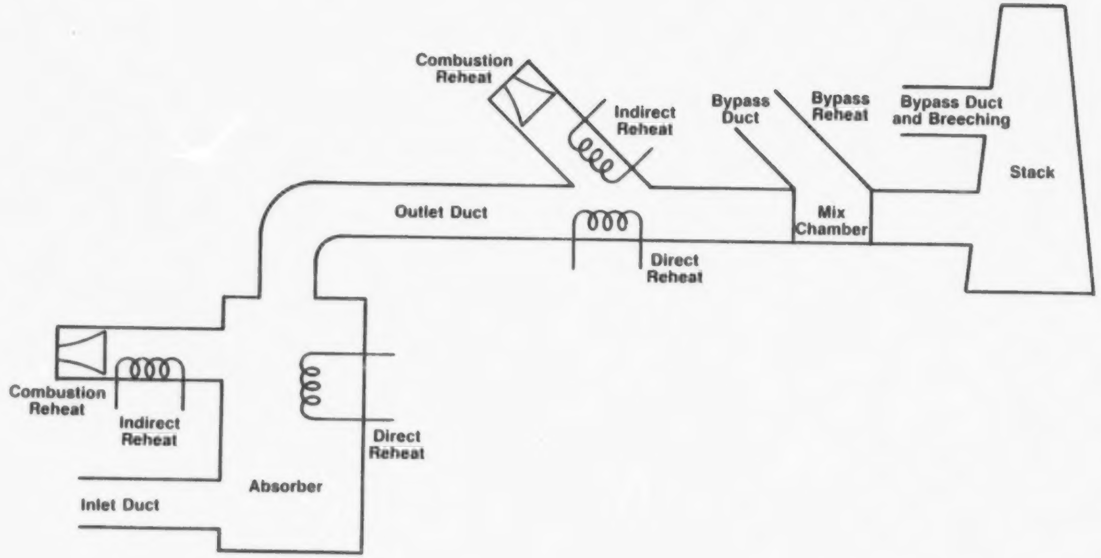
The performance of an outlet duct material or lining depends upon the environmental conditions within the duct. The outlet duct is exposed to saturated (wet) flue gas at about 125 F (52 C) and/or reheated flue gas at about 140 to 180 F (60 to 82 C) depending upon the existence and location of a reheat system (refer to Figure 1). Part of the outlet duct may also be exposed to hot flue gas at about 300 F (149 C) during periods of shutdown of the FGD system if a bypass duct joins the outlet duct ahead of the stack. Although application conditions and procedures are important to the success of a lining, this fact has perhaps been overemphasized by suppliers.

The outlet duct has been a major problem area, particularly for FGD systems which have duct sections that handle both wet gas and hot gas. Environmental conditions developed during scrubber operation can become more severe with bypass as the temperature is raised and additional corrosive species in the unscrubbed flue gas (chloride and fluoride as well as SO_x and NO_x) are introduced. Because a failure of the outlet duct in this area can require shutdown of the boiler while repairs are made, it is important to use long lasting linings and/or alloys.

STACKS

The flue gas from an FGD system exits to the atmosphere through a chimney or stack. The stack consists of an outer shell constructed of concrete or carbon steel and one or more flues constructed of brick, metal, or fiberglass-reinforced plastic (FRP) which carry the flue gas (refer to Figure 2) (3). The interior surface of the flue is subjected to the flue gas conditions and therefore, as with outlet ducts, provisions must be made for protection against deterioration or corrosion.

The performance of a stack lining depends on whether the scrubbed gas is delivered to the stack wet or reheated (refer to Figure 1), and whether or not the stack is also used for hot bypassed gas. These factors may have a stronger effect on the performance of lining materials than differences in fuel sulfur content, application techniques (e.g., surface preparation or priming), operating procedures (e.g., thermal shock), design aspects (e.g., annulus pressurization), and other factors which can affect performance.


Combustion Reheat
Indirect Reheat
Bypass Duct
Bypass Reheat
Bypass Duct and Breeching
Stack
Outlet Duct
Mix Chamber
Direct Reheat
Combustion Reheat
Indirect Reheat
Direct Reheat
Absorber
Inlet Duct

	Direct Reheat	Indirect Reheat	Combustion Reheat	Bypass Reheat	No Reheat
Examples	Reheat in Scrubber Vessel Mill Creek 3	Reheat in Scrubber Vessel Widows Creek 8	Reheat in Scrubber Vessel Paddy's Run 6	Mix in Duct Gibson 5*	Bypass to Duct Duck Creek 1*
	Reheat in Outlet Duct Cane Run 5	Reheat in Outlet Duct San Juan 1&2* Gibson 5*	Reheat in Outlet Duct Cane Run 4	Mix in Stack Dallman 3	Bypass to Stack Southwest 1
	*Included in this paper.				No Bypass Bruce Mansfield 3* Phillips*

Figure 1. Type and location of flue gas reheat systems.

Although acid-resistant brick linings have exhibited good performance in all categories of operating conditions, a leaning phenomenon (eccentricity in the annular space between the flue and the shell) has recently been reported for several free-standing brick flues. This phenomenon has required some utilities to do considerable maintenance work near the top of the stack to eliminate rain cap rubbing and/or provide adequate clearance to accommodate wind load deflections of the concrete shell. In one case, the flue was completely rebuilt with different type bricks having lower water absorption and with the same type mortar, but from a different supplier. Because of the relative importance of the problem, operating experience and construction details were compiled for about 50 free-standing brick flues on wet FGD systems at electric utilities. This information, as well as possible explanations for the leaning phenomenon, has been presented in a previous publication (4).

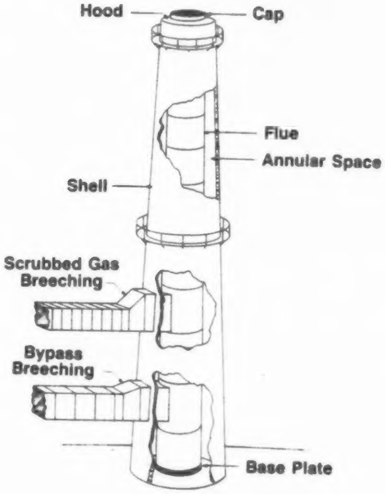


Figure 2. A typical stack (3).

PERFORMANCE ANALYSIS

As part of the current study on materials failure causes in FGD systems, Battelle analyzed the field performance of two outlet duct linings and three stack materials. The outlet duct linings included a glass-flake-filled polyester at San Juan and an hydraulic-setting, calcium aluminate cement-bonded concrete at Gibson. The stack materials included a mica-flake-filled polyester at Duck Creek, an Alloy 625 flue at Bruce Mansfield 3, and an acid-resistant brick and mortar flue at Phillips. Information on the performance of these stack linings has been presented in a previous publication (4). It should be noted with regard to the stack materials that only the lining at Duck Creek represented an actual failure.

A team consisting of personnel from Battelle's Columbus Laboratories and Black & Veatch Engineers-Architects visited each site during a boiler shutdown. Black & Veatch assisted as a subcontractor in providing expertise in the engineering design of FGD systems. The purpose of the visits was to (1) interview plant personnel, (2) inspect the outlet duct or stack, and (3) collect samples of the lining, where appropriate, for detailed analysis. Condensate samples were collected by plant personnel when the FGD system was in operation. The lining samples were analyzed using various techniques including optical microscopy, scanning electron microscopy/energy dispersive X-ray spectroscopy, X-ray diffraction, and infrared spectroscopy. The results were used to evaluate the performance of the linings.

OUTLET DUCT LININGS

Glass-Flake-Filled Polyester Lining at San Juan Station

The San Juan Generating Station is located 14 miles northwest of Farmington, New Mexico, and consists of four coal fired units. The station is jointly owned by Public Service Company of New Mexico (PSNM) and Tucson Gas and Electric and is operated by PSNM. Units 1 and 2 have Foster Wheeler pulverized coal fired boilers rated at 314 and 306 MW, respectively, and use New Mexico coal containing about 0.8 percent sulfur, 22 percent ash, and 15 percent moisture. Wellman-Lord FGD systems were installed as retrofits on Units 1 and 2 and at the time of construction of Units 3 and 4. The FGD systems consist of four absorber modules for each unit, each module having a dedicated booster fan. Normally, three of the four modules are in operation at any one time. The FGD system on Unit 1 started up in April, 1978, using two modules, and on Unit 2 in September, 1978, with three modules. It was necessary to operate two out of four modules on each unit through mid-1980 to meet the SO_2 emission regulations. Thereafter, three of four modules had to be in operation to meet more stringent regulations.

Fly ash is removed in hot-side electrostatic precipitators having efficiencies of 99.8 percent on Unit 1 and 99.5 percent on Unit 2. The hot flue gas, containing small quantities of fly ash, is then directed to combustion air preheaters, to the booster fans, and then on to venturi scrubbers where it is quenched with river water. The flue gas is then contacted with a sodium sulfite liquor in the absorbers to remove SO_2 and exits to the stack. Flue gas reheat is provided by hot air injection from an indirect steam coil reheater. The SO_2 is removed from the spent scrubbing liquor by evaporation and is converted to sulfuric acid. The design SO_2 removal efficiency from the flue gas is approximately 90 percent.

The outlet ducts for each absorber vessel are oriented vertically and feed to a single horizontal plenum. These ducts and the plenum on Units 1 and 2 are all fabricated of carbon steel with a glass-flake-filled polyester lining. A horizontal duct, fabricated of Type 316L stainless steel (2.75 percent Mo), connects the plenum to the stack and contains the mixing zone for the indirect hot air reheater. A simplified gas flow diagram is shown in Figure 3.

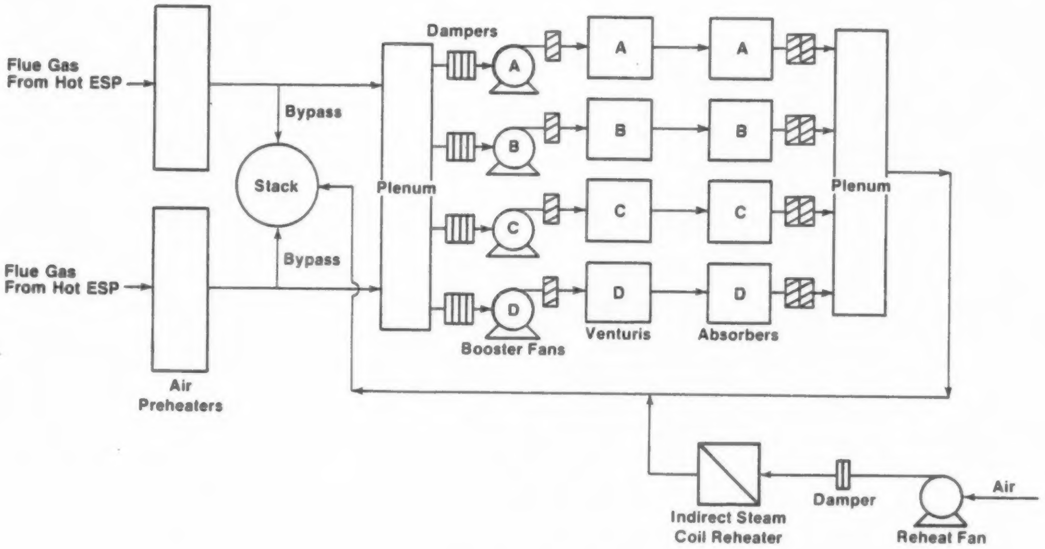

Flue Gas From Hot ESP
Flue Gas From Hot ESP
Air Preheaters
Bypass
Bypass
Stack
Plenum
Dampers
A
B
C
D
Booster Fans
A
B
C
D
Venturis
A
B
C
D
Absorbers
Plenum
Indirect Steam Coil Reheater
Damper
Reheat Fan
Air

Figure 3. Simplified gas flow diagram for San Juan Unit 1 or 2.

Debonding failures of the lining in the outlet duct on Units 1 and 2 have occurred so that periodic relining is required. The internal ductwork bracing was carbon steel pipe covered with the same lining material as the outlet duct, but was replaced with bare Type 316 stainless steel pipe in early 1984 because of corrosion problems due to debonding of the lining.

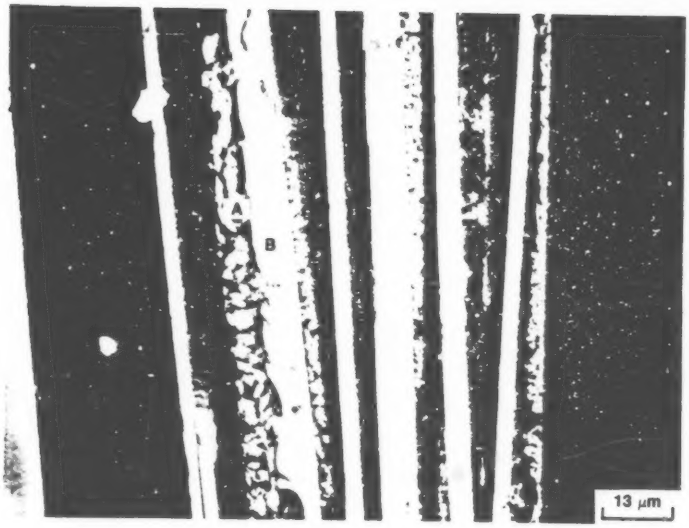
Battelle and Black & Veatch inspected the outlet duct on Unit 1 in October, 1983. Evidence of serious debonding of the lining was found on the roof, the upper portion of the plenum walls, the turning vanes, and the internal duct bracing. The bracing at the top of the plenum appeared to be in the worst condition. Corrosion of the bracing was severe and one brace had broken away from both end connections and lay on the ductwork floor. The lining on the lower portion of the walls and on the floor appeared to be in good condition.

Deposit and lining samples were taken from the internal bracing and from turning vanes located at floor level between the outlet plenum and the horizontal duct. All of the samples were taken from areas where the lining had debonded and, thus, were easily removed from the substrate. The samples were covered with gray-black deposits on the surfaces which faced the flue gas and rust red deposits on the surfaces which faced the carbon steel. Lining samples were not taken from the plenum walls since it had not been decided whether the walls were to be repaired during the outage.

The lining samples were metallographically mounted and analyzed with a scanning electron microscope. The results indicated that iron, sulfur, and sodium had diffused into the lining. The iron probably originated from fly ash, the sulfur from SO_2 in the flue gas, and the sodium from scrubbing liquor carryover. A high iron concentration was also found near the bottom surface of the lining, probably from corrosion of the carbon steel substrate. A high magnification photomicrograph indicated the presence of deposits on the glass flakes (refer to Figure 4). Energy dispersive X-ray analysis of the deposits indicated high concentrations of sodium and sulfur on glass flakes near the top surface and high concentrations of iron and sulfur on glass flakes near the carbon steel substrate.

X-ray diffraction analysis of a lining sample indicated the presence of natrojarosite [$NaFe_3(SO_4)_2(OH)_6$] and parabutlerite [$FeSO_4(OH)\cdot 2H_2O$]. Natrojarosite is a highly insoluble compound that can be formed by reaction of ferric sulfate with sodium sulfate at low pH and temperatures around 140 F (60 C) (5). The conditions for forming this compound exist on the duct wall. Iron is available from the fly ash and/or the duct substrate, sulfur from the flue gas, and sodium from the scrubbing liquor carryover from the mist eliminator. The fact that sodium, iron, and sulfur were not found together in the deposits on the glass flakes may be explained by the precipitation of natrojarosite on the top surface of the lining. This may also explain why iron is not present in the deposits near the top surface; presumably, these deposits are sodium sulfate. Near the bottom surface of the lining, the sodium concentration was low so that the migration of iron from the substrate apparently was not hindered by the formation of natrojarosite. The deposits near the bottom surface may be parabutlerite. Because of the different composition of the deposits near the top and bottom surfaces of the lining, it appears that the glass flakes did not participate in the reaction which produced the deposits (i.e., the glass flakes were not attacked), but simply provided sites for precipitation or possibly catalyzed the reaction.

The most probable cause of failure of the lining is heat damage due to back mixing of hot air at about 400 F (204 C) from the reheat zone and/or



	w/o	
Element	Point A	Point B
Na	25.1	6.1
Mg	—	2.2
Al	—	4.1
Si	—	62.1
S	74.9	—
Ca	—	24.2
Fe	—	1.3

Point A is in a deposit and Point B is in a glass flake.

Figure 4. Cross section of glass flakes and deposits within San Juan outlet duct lining (scanning electron photomicrograph).

bypassed gas at about 275 F (135 C) from the stack. This overheating may have promoted debonding of the lining because of the difference in thermal expansion between the lining and the substrate. Alternately, overheating may have promoted lining failure by degradation of the polyester resin or by deposition of solids on the glass flakes. Although it is not conclusive that the presence of the deposits promoted or even contributed to the lining failure, it is clear that their formation is undesirable. The volume change associated with their formation probably would eventually promote internal cracking of the lining or delamination at the lining-metal interface, although evidence of these failure modes was not found; a more complete failure analysis was not possible because of the inability to obtain samples which contained sections of the metal substrate. Moreover, the presence of the deposits, at the very least, is an indication that the lining is not performing as an adequate barrier to the ingress of deleterious species present in the flue gas and flue gas condensate. The presence of sulfur in the deposits near the substrate is indicative of sulfurous and/or sulfuric acid diffusion into the lining. This can cause acid hydrolysis of the polyester and/or debonding of the lining because of corrosion of the carbon steel substrate.

Calcium Aluminate Cement-Bonded Concrete Lining at Gibson Station

Gibson Station of Public Service Indiana is located on the Wabash River in southwestern Indiana. Unit 5 is rated at 650 MW and burns 3.3 percent sulfur coal. The unit has electrostatic precipitators for fly ash removal and a wet limestone FGD system for SO_2 removal. The FGD system operates in a closed-loop mode and consists of four horizontal spray absorbers which utilize magnesium-promoted (dolomitic lime additive) limestone slurry. One of the modules is a spare and each module is designed to treat 28 percent of the flue gas with 16 percent bypass for reheat in the outlet duct mixing zone. Partial or full bypass is also possible through two main bypass ducts to the stack. There is an indirect steam coil reheater for hot air injection into the outlet duct, but it has not been used. A simplified gas flow diagram is shown in Figure 5.

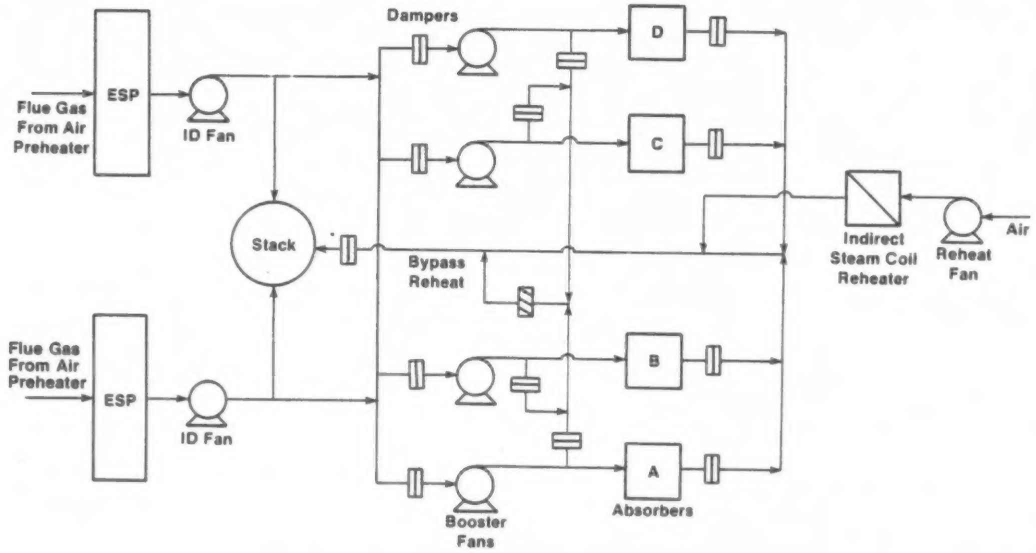

Dampers
D
C
Flue Gas From Air Preheater
ESP
ID Fan
Stack
Bypass Reheat
Indirect Steam Coil Reheater
Reheat Fan
Air
B
Flue Gas From Air Preheater
ESP
ID Fan
A
Absorbers
Booster Fans

Figure 5. Simplified gas flow diagram for Gibson Unit 5.

Gibson 5 has been in operation since October, 1982. The load cycles from about 600 MW during the day to about 250 MW at night. Consequently, three modules are typically in use during the day, but only two are required at night, causing a daily operational cycle for one of the four modules.

The outlet ducts from the absorber modules are horizontal to the reheat zone where the common duct slopes upward to the stack breeching. The carbon steel ducts are outdoors and are not insulated. They are lined with an hydraulic-setting, calcium aluminate cement-bonded concrete (gunite) from the absorbers to the breeching. The 1-in. (25 mm) thick gunite was applied to 2 in. x 2 in. x 12 gage (50 mm x 50 mm x 2.8 mm) mild steel welded wire mesh held 1/2 in. (13 mm) from the wall. There is a coal tar epoxy membrane between the gunite and the steel duct only on the floor and 2 ft (0.6 m) up the wall.

The outlet ducts from Modules A and D have exhibited gunite deterioration just downstream from the right-angle elbows near the outlet isolation dampers (refer to Figure 5). This deterioration was not as severe or rapid in the outlet ducts from Modules B and C, and has not occurred in the downstream reheat mixing zone. When Module A or D is isolated, backflow of flue gas into the stagnant section of the outlet duct may be causing increased condensation and attack. When Module B or C is isolated, there is no comparable stagnant outlet duct section.

Battelle and Black & Veatch inspected the outlet duct in April, 1984. The gunite lining was covered with a dense, continuous, adherent scale except for the stagnant end sections where the scale was discontinuous. In the latter sections, gunite deterioration and/or erosive wear had occurred up to the depth of the wire mesh reinforcement. The deterioration was evident as a powdering of the top layer of the lining. The scale had not yet been removed in the outlet duct from Module A so that full-depth lining samples could be obtained for laboratory analyses. In the Module D outlet duct, the scale had been removed by water blasting which had exposed the wire mesh in some areas. In most areas, the wire mesh was still covered with gunite, but the lining had eroded away in a manner that revealed the mesh pattern within the material. This suggests that the mesh interfered with the gunning procedure during application of the lining and caused slight variations in lining properties above and between the wires. Samples of sound lining were carbide drilled from between the mesh for laboratory analyses.

X-ray diffraction analyses of the lining samples as a function of depth indicated the presence of gypsum ($CaSO_4 \cdot 2H_2O$) in the deteriorated layer, but not in the bottom layer. Several other compounds were identified including quartz (SiO_2), anorthite [$(CaO,Na_2O) \cdot Al_2O_3 \cdot 2SiO_2$], gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$), and gibbsite ($Al_2O_3 \cdot 3H_2O$), but unlike gypsum, these species are also present in unexposed lining samples. However, the analyses indicated a depletion of the gibbsite toward the surface of the lining samples from Module A.

Energy dispersive X-ray analyses of the Gibson lining samples confirmed that aluminum had been leached from the deteriorated layer of the lining. The calcium content of the degraded portion of the lining was about the same as that in the bottom portion of the lining. The sulfur content of the degraded portion was about 10 times higher than in the bottom portion of the lining. The sulfur content in the bottom layer of the lining was comparable to that of unexposed lining samples, indicating little or no penetration of condensate with ionic sulfur species beyond the zone of visible degradation. The concentration profiles for aluminum, calcium, and sulfur are shown in Figure 6.

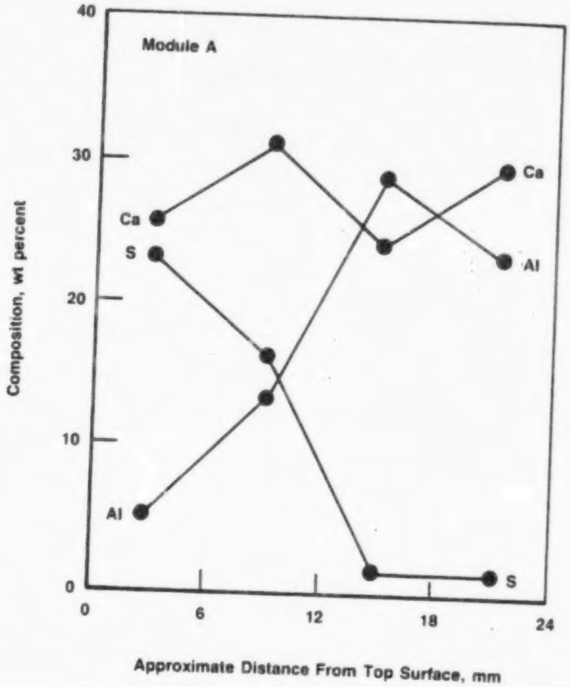


Figure 6. Concentration profiles in Gibson outlet duct lining.

A condensate sample taken from the outlet duct drain under full load operation was found to have a pH of about 2.5. The results of a chemical analysis of the condensate are shown in Table 1 along with an analysis of the scrubbing liquor. The calcium concentration in the condensate corresponds approximately to that of a saturated solution of calcium sulfate. The calcium can result from carryover of scrubbing liquor from the mist eliminator or from leaching of the duct lining. The latter is thought to be more likely on the basis of a comparison of condensate to scrubbing liquor concentration ratios shown in Table 1. Magnesium and chlorine have about the same low ratio and are likely present because of mist eliminator carryover. The ratio for calcium is much higher. Aluminum can originate from fly ash carry-over as well as from leaching of the duct lining. The latter is more likely on the basis of a comparison with the iron concentration in the condensate. If the aluminum were mainly from the fly ash, the iron concentration, which is also due to fly ash, should be higher as indicated at other FGD installations (6,7). The major source of sulfate in the condensate is most likely residual SO_x remaining in the scrubbed flue gas.

TABLE 1. ANALYSES OF OUTLET DUCT CONDENSATE AND SCRUBBING LIQUOR FROM GIBSON UNIT 5

Species	Concentration, mg/l		Ratio of Condensate to Scrubbing Liquor Analysis
	Condensate	Scrubbing Liquor	
Cations			
Al	530	NA*	
Ca	730	550	1.33
Fe	86	NA	
K	39	NA	
Mg	400	8,000	0.05
Na	26	NA	
Si	22	NA	
Anions			
Cl	320	6,000-12,000	0.03--0.05
F	17	NA	
SO_3	NA	4,000	
SO_4	6,300	20,000	0.32
pH	2.5	5.3	

*Not analyzed.

The results obtained in this investigation indicate that gypsum formation in the gunite lining caused the lining to deteriorate. Gypsum formation was probably due to reaction between dilute sulfuric acid in the duct condensate and calcium originally present in the lining rather than precipitation from the condensate. The condensate that permeated the lining had a maximum pH of about 2.5 and leached $Al_2O_3 \cdot 3H_2O$ from the lining, probably because of acid attack. According to its manufacturer, the gunite lining in the outlet duct at Gibson will resist sulfuric acid down to a pH of about

3.5 in immersion service, but it is not intended for use under the more acidic conditions that have been encountered.

STACK LININGS

Mica-Flake-Filled Polyester Lining at Duck Creek Station

The Duck Creek Generating Station of Central Illinois Light Company is located in an unreclaimed strip mine area near Canton, Illinois. Duck Creek 1 is rated at 416 MW and designed for firing high sulfur coal. The emission control system consists of electrostatic precipitators for fly ash removal and a wet limestone, closed-loop FGD system for SO_2 removal. A simplified gas flow diagram is shown in Figure 7.

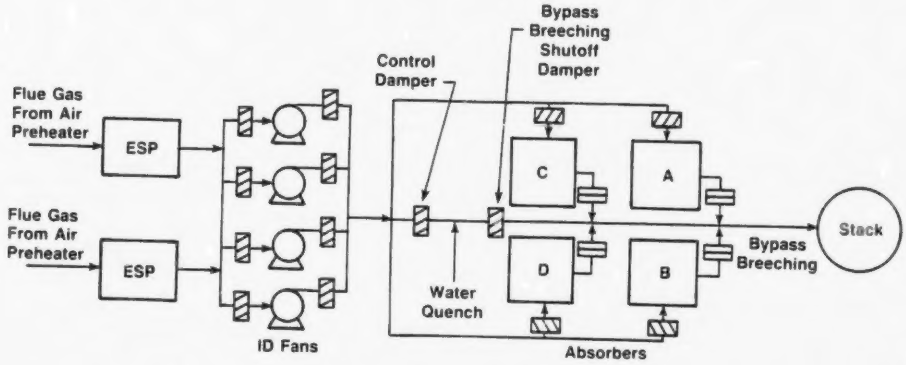

Bypass
Breeching
Shutoff
Damper
Control
Damper
Flue Gas
From Air
Preheater
ESP
Flue Gas
From Air
Preheater
ESP
C
A
D
B
Stack
Bypass
Breeching
Water
Quench
ID Fans
Absorbers

Figure 7. Simplified gas flow diagram for Duck Creek Unit 1.

A system of four induced draft fans is connected to a common duct that distributes the flue gas to either the bypass breeching or the FGD system. The bypass breeching, which can accommodate any or all of the flue gas, consists of a straight duct extending from the fan system to the base of the stack. The flue gas can be routed to any or all of the four absorbers by a series of dampers. A flue gas quenching system is located in the bypass breeching just downstream from the bypass control damper. When operating in the full or partial bypass mode, the quenching system is used in an attempt to maintain the gas temperature entering the stack between 248 and 284 F (120 and 140 C).

The unit began operation in 1976, several months ahead of completion of the FGD system. One absorber module was placed in service (only one module had been constructed) in July, 1976, and operated intermittently through the remainder of the year. From April, 1977, to August, 1978, low sulfur coal was burned while design changes were made to the FGD system and three additional modules were constructed. Commercial start-up occurred in August, 1978.

The stack at Duck Creek is 500 ft (150 m) high and has a concrete shell and a carbon steel flue with a single breeching. The original flue lining was a mica-flake-filled polyester with an average thickness of 0.2 in. (5 mm). The lining was applied in two coats, a base coat and a top coat, the base coat having a higher density of mica flakes. After the first six months of operation with only one absorber module in service, the entire top coat of the lining had failed. The system was continued in operation with only the base coat lining, even after all four absorber modules went on line. A major boiler outage took place in late 1981 and, after restarting, failure of the base coat was observed. Chunks of the lining were heard falling continuously onto the hopper at the bottom of the stack. In April, 1982, a 100 ft (30 m) section [from the 115 ft (35 m) level, approximately 6.5 ft (2 m) below the expansion joint, to the 220 ft (67 m) level] was replaced with another mica-flake-filled polyester similar to the base coat of the original lining, and with an average thickness of approximately 0.2 in. (5 mm). Considerable blistering and cracking of the replacement lining was observed during an inspection in February, 1983. The flue lining was completely removed in May, 1983, and the steel was repaired and relined with an epoxy filled with fiberglass and glass beads.

Battelle and Black & Veatch inspected the flue at the end of February, 1983, and obtained samples of both polyester linings. Inspection ports were opened at the 150 ft (46 m) and 288 ft (88 m) levels so that both linings could be examined closely. From the inspection ports, it could be seen that the upper part of the original flue lining had completely debonded from the substrate, exposing the bare carbon steel. Many pieces of the lining had fallen to the bottom of the stack. At the lower section of the flue up to about 197 ft (60 m), the replacement lining showed some blistering and debonding. A sample of each lining was obtained by using a torch to cut two one ft (0.3 m) diameter carbon steel disks from the flue.

Optical photomicrographs of cross sections through the polyester linings showed debonding within the lining (cohesive failure) and debonding along the lining-substrate interface (adhesive failure). The original lining showed extensive cohesive and adhesive failure, but it could not be determined whether failure had initiated at the lining-steel interface or within the lining. However, the replacement lining showed primarily cohesive failure, suggesting that lining deterioration rather than debonding from the substrate was the predominant mode of failure.

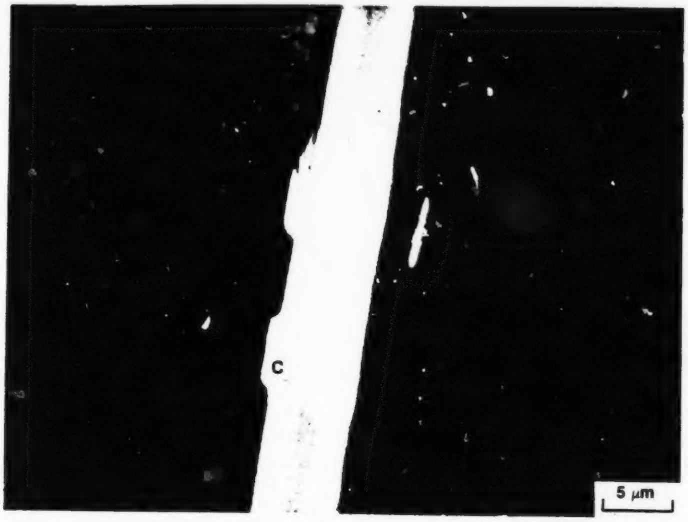
A sample of each lining was removed from the carbon steel substrate to obtain infrared spectra from the surface facing the flue gas (top surface) and the surface facing the substrate (bottom surface). The spectra obtained from the top surface of both linings showed few differences, suggesting that the same polyester resin was in both linings. However, when these spectra were compared, a higher level of sulfate was indicated in the original lining. This would suggest that the original lining was exposed to a large quantity of sulfur-containing species, which is consistent with the longer exposure time of this lining.

Comparison of the spectra from the top and bottom surfaces of each lining showed that in both cases a radical change had occurred in the lining. The spectra from the top surface of both linings showed only a trace of an ester, whereas the spectra from the bottom surfaces exhibited a much higher concentration of R-COOR groups. Since acid hydrolysis of a linear polyester occurs in the ester linkage, these spectra indicated that considerable hydrolysis had occurred on the exposed surface of the polyester in both linings.

X-ray diffraction analysis of the linings indicated that the overwhelmingly predominant compound in the original lining was ammoniojarosite [$NH_4Fe_3(SO_4)(OH)_6$], while the replacement lining contained mica (muscovite-$K_2O_3 \cdot Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$) and jarosite [$KFe_3(SO_4)_2(OH)_6$]. The conditions for forming the highly insoluble jarosites exist on the flue wall as discussed previously. Iron is available from the fly ash and/or the flue substrate, sulfur from the flue gas, and potassium from the mica flakes. The source of ammonia was a mystery until it was learned that a material containing ammonium sulfate had been injected into the flue gas from late 1976 to 1978 to condition the electrostatic precipitator. The formation of jarosites could have contributed to the lining failure.

The cross sections cut from both polyester linings samples were analyzed with a scanning electron microscope. The results indicated that iron and sulfur had diffused into the linings. A high magnification photomicrograph of the replacement lining indicated the presence of deposits on the mica flakes (refer to Figure 8a). Energy dispersive X-ray analysis of the deposits indicated high concentrations of iron, sulfur, and potassium. Sulfur X-ray mapping of the area showed sulfur concentration at the deposits (refer to Figure 8b). These observations are consistent with the presence of jarosite in the deposits. It can be speculated that iron and sulfur which diffused into the lining formed the jarosite with potassium from the mica. Since jarosite is very insoluble, it would form immediately at the interface. The jarosite deposits may have caused debonding between the mica flakes and the resin and, eventually, total failure of the lining. Although alunite [$K_2Al_3(SO_4)_2(OH)_6$] was not detected by X-ray diffraction, this compound may also have formed, as evidenced by the presence of aluminum in the deposits, and contributed to lining failure.

The results obtained in this investigation indicate that the original lining failed as a result of acid hydrolysis, and by the formation of ammoniojarosite and possibly alunite, which caused extensive debonding of the lining. Temperature cycling between ambient and about 140 F (60 C) as a result of repeated start-ups and shutdowns probably increased the rate of precipitation of ammoniojarosite and alunite. Subsequently, the lining also



Element	Point C, w/o
Mg	7.66
Al	11.7
Si	18.2
S	18.98
K	12.75
Ti	1.79
Fe	28.91

Point C is in a deposit.

Figure 8a. Cross section of mica flake with deposits within Duck Creek flue lining (scanning electron photomicrograph).

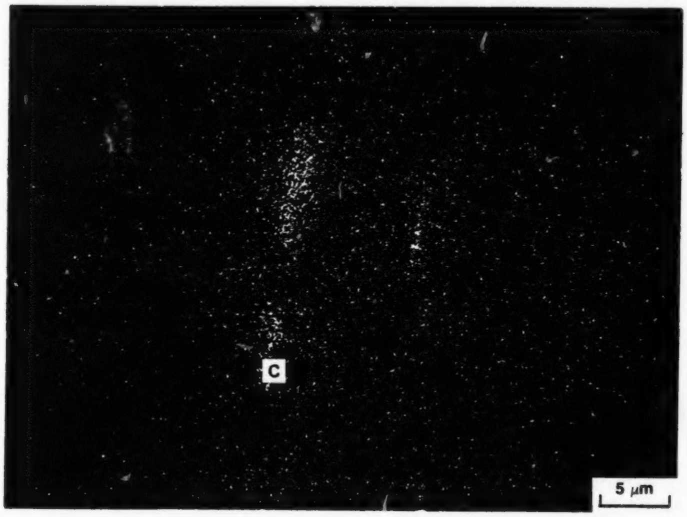


Figure 8b. Sulfur X-ray map of same area shown in Figure 8a.

deteriorated by ingress of water and acid. The replacement lining, which was in service for only about one year, showed resin failure by acid hydrolysis. Also, buildup of jarosite possibly wedged the mica flakes and resin apart causing cohesive failure and, eventually, blister formation.

High Nickel Alloy Flue at Bruce Mansfield Station

The Bruce Mansfield plant of the Pennsylvania Power Company is located on the Ohio River near Shippingport, Pennsylvania. Unit 3 is rated at 825 MW and is designed to be fired with 4.3 percent sulfur coal. The unit started up in April, 1980, and went commercial on September 29, 1980. The FGD system consists of four electrostatic precipitators connected in parallel, followed by five horizontal spray scrubbers, one of which is a spare. The scrubbers use a slurry of magnesium-promoted lime to remove SO_2 and residual fly ash and operate in an open-loop mode. The flue gas exits the scrubbers to a common outlet duct and stack. The stack contains two flues 19 ft (5.8 m) in diameter by about 600 ft (183 m) high. There is no bypass of the FGD system and no flue gas reheat. A simplified gas flow diagram is shown in Figure 9.

The flues are made of Alloy 625. They were fabricated by welding three cylindrical plates 5 ft x 20 ft x 0.25 in. (1.5 m x 6.1 m x 6.4 mm) to form a ring. Two rings were welded together on the ground and the resulting 10 ft (3 m) high ring was welded to the bottom of the flue. The flue was then raised and a new 10 ft (3 m) high ring was positioned and welded in place. Thus, the initial welds are located at the top of the flue.

An examination of flue 3A was performed on March 27, 1984, using a float erected by Peabody-Holmes. The latter company had also removed and accumulated flue deposits with scraper bars prior to Battelle's inspection. The work by Peabody-Holmes was the first detailed inspection and cleaning of the flue since start-up. Battelle and Black & Veatch inspected the inside of the flue from the duct breeching to the top of the stack. Ultrasonic wall thickness measurements, which had been made by Peabody-Holmes and indicated on the wall, were recorded and the depth of any localized attack found was measured with calibrated gauges. Samples of the flues were not obtained because there was no failure of the material.

There had been considerable scale buildup, up to 9 in. (0.23 m) thick on the lower portion of the flue [95 ft (29 m) elevation above grade], but the scale thickness decreased with increasing elevation and no scale was found above the 300 ft (90 m) level. The deviation in wall thickness based on four readings around the circumference at a given elevation ranged from 6 mils (0.15 mm) to 24 mils (0.61 mm) and was random with elevation.

There was evidence of considerable mechanical damage on the surface of the flue, some of which probably resulted from the removal of deposits. In addition, there were numerous weld strikes and grinding marks near the welds; in general, the weld relief was not ground off. The weld quality was very good near the bottom of the stack, but deteriorated with increasing

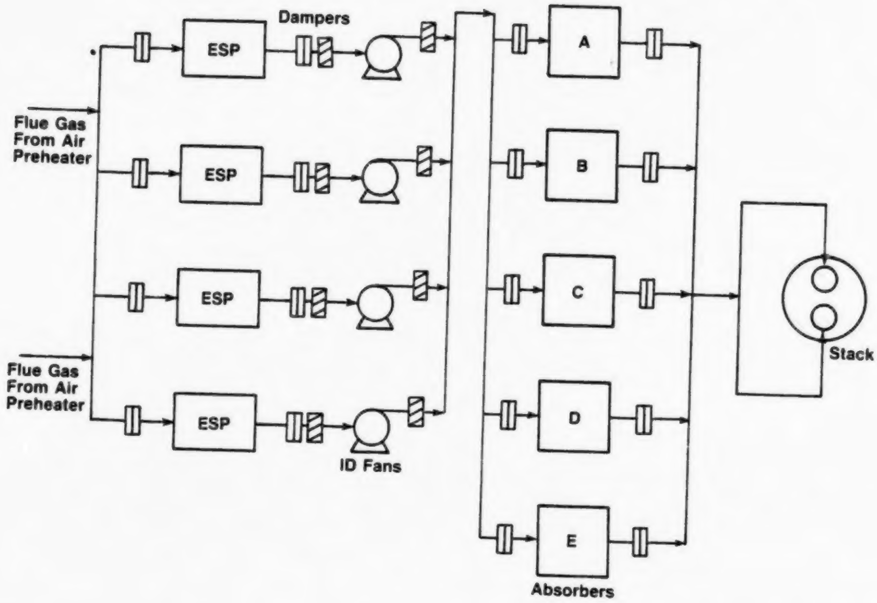

Dampers
ESP
ESP
ESP
ESP
Flue Gas From Air Preheater
Flue Gas From Air Preheater
ID Fans
A
B
C
D
E
Absorbers
Stack

Figure 9. Simplified gas flow diagram for Bruce Mansfield Unit 3.

height. At the top of the stack, there was considerable weld splatter, porosity, undercutting, and numerous crevices. Since the top portion of the stack had been welded first, it appears that the weld quality improved with increasing experience gained by the welders.

In spite of the presence of numerous potential sites for initiation of corrosion, there was no evidence of significant attack in the bottom two-thirds of the flue. Near the top of the stack, apparent crevice corrosion, about 10 mils (0.25 mm) deep, was observed on several plates. However, because it was confined to specific plates and no scale buildup occurred, this apparent attack may actually be pre-existing defects resulting from poor processing of the plates. Several dark patches approximately 3 in. (76 mm) in diameter were observed in the same general area; small pits, less than 10 mils (0.25 mm) deep, were located within these patches.

This investigation indicated that the Alloy 625 flue had performed very well over the 4-year operating period. The material exhibited good performance in spite of the presence of thick deposits which can produce detrimental crevice conditions, many weld defects, and areas of heat tint and mechanical damage. However, this flue is subjected only to wet flue gas; the performance of the same material under more severe environments such as a mixture of wet gas and hot gas might not be the same.

Acid-Resistant Brick and Mortar Flue at Phillips Station

The Phillips Station of the Duquesne Light Company is located near Pittsburgh in South Heights on the Ohio River. The station burns coal with about 2 percent sulfur and has a retrofit FGD system with single stage venturi scrubbers using lime slurry. There are six boilers (387 MW total) with four absorber modules with no bypass duct and no flue gas reheat. Although improvements have been made in the water balance, the FGD system still operates in an open-loop mode occasionally. The plant has a stack with one flue and a single breeching. A simplified gas flow diagram for Phillips is shown in Figure 10.

Scrubber operations began in 1973 with flue gas from three boilers, and all six boilers were connected to the FGD system by 1975. The plant originally started operation using high purity lime, but switched to magnesium-promoted lime (containing 8 to 9 percent MgO) in 1977 for improved SO_2 removal. In 1980, the addition of sodium thiosulfate (a sulfite oxidation inhibitor) to the FGD system was initiated to reduce sulfate scaling problems.

The stack is 340 ft (104 m) high and has a concrete shell with a free-standing brick flue. The flue is constructed of Type L red shale bricks and potassium silicate mortar. The flue thickness ranges from 16 in. (0.41 m) at the bottom to 8 in. (0.20 m) at the top. The stack is somewhat unusual in that the base of the flue is located on a floor cast across the shell about 80 ft (24 m) above ground level. A single breeching enters the flue about 10 ft (3 m) above the floor. The stack has a rain cap above the annular space.

The station has had seepage of condensate through the brick flue, resulting in salt crystal growth on the annulus side and corrosion of the reinforcing bands and light fixtures. The original mild steel bands were replaced with Type 316 stainless steel bands during the first year of operation, and, in late 1983, the latter bands were replaced with Alloy 625. Minor repairs have also been done to the base of the stack on the inside to prevent seepage through the acid-resistant brick floor. Because the band corrosion problem was so severe, the annulus was pressurized in late 1982, but by late 1983, as much as 1/4 in. (6.4 mm) of new salt deposits had reformed. Before pressurization, these deposits had gotten as thick as 4 in. (100 mm) during the periods between band replacements. While annulus pressurization has helped, it has not eliminated the condensate permeation problem. The stack does not lean nor has it exhibited permanent vertical growth.

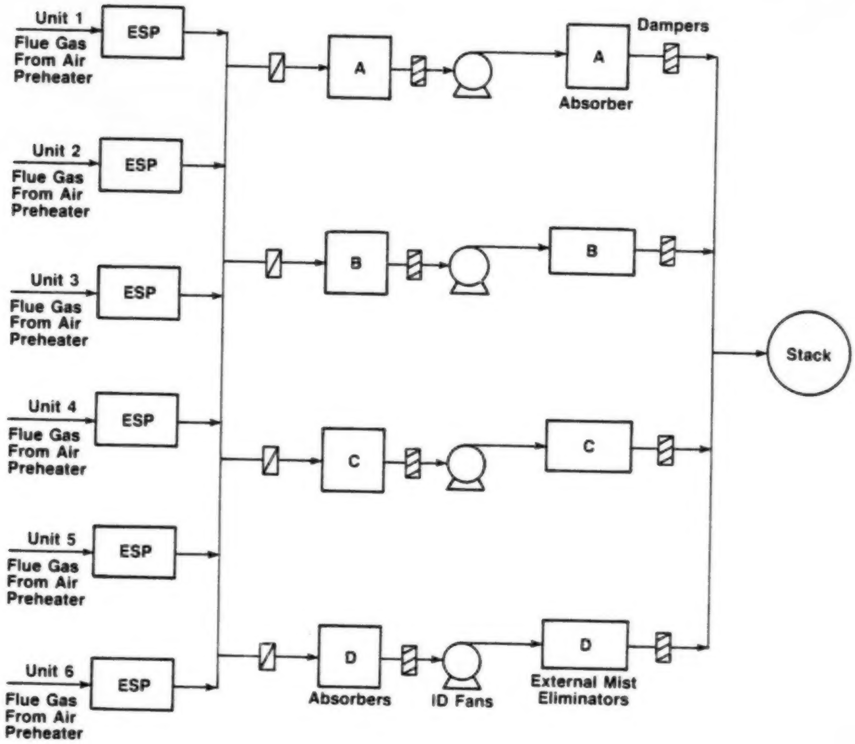

Unit 1
Flue Gas From Air Preheater
Unit 2
Flue Gas From Air Preheater
Unit 3
Flue Gas From Air Preheater
Unit 4
Flue Gas From Air Preheater
Unit 5
Flue Gas From Air Preheater
Unit 6
Flue Gas From Air Preheater
ESP
A
B
C
D
Absorbers
ID Fans
Dampers
Absorber
External Mist Eliminators
Stack

Figure 10. Simplified gas flow diagram for Phillips Station.

Battelle and Black & Veatch first inspected the flue in November, 1983. The flue could be inspected only at the base on the annulus side because the station was in operation. Salt deposits which were heaviest at the mortar joints were observed. Most of the joints appeared to be filled with mortar. Moisture from seepage was observed in several areas. Salt samples were obtained for analysis. A subsequent visit was made in April, 1984, to inspect the interior of the flue during an outage. The surface had a 1/32 in. (0.79 mm) layer of fly ash, but the bricks and mortar appeared to be in good condition. Mortar and brick samples were drilled from the interior of the flue and mortar samples were taken from the annulus side, both near the base.

The condensate collected in the stack was analyzed and the results are summarized in Table 2. The condensate was acidic and contained typical values for sulfate, chloride, and fluoride (8). The source of magnesium is probably the lime.

TABLE 2. ANALYSES OF STACK CONDENSATE FROM PHILLIPS STATION

Species	Concentration, mg/l
Cations	
Al	5.5
Ca	75
Fe	4.4
K	26
Mg	190
Na	27
Si	11
Anions	
Cl	120
F	59
SO_4	1,200
pH	2.6

X-ray diffraction analysis of the salt deposits from the flue indicated the presence of hexahydrite ($MgSO_4 \cdot 6H_2O$) and/or gypsum ($CaSO_4 \cdot 2H_2O$) in all samples. Other forms of magnesium sulfate were observed in one or two cases. The ratio of gypsum to magnesium salts was high, which is surprising in view of the low solubility of the former and the roughly equal concentrations of calcium and magnesium found in the condensate.

Two of the salt deposit samples were leached in water and the water was analyzed for fluorides, chlorides, and sulfates. The results showed high sulfate, some fluoride, and little or no chloride. The sulfate/fluoride ratio was about the same as in the stack condensate. Thus, fluorides appear to be permeating through the flue and may contribute to the corrosion of the metal bands in the annulus. The absence of chlorides indicate that either chlorides are not permeating through the flue or they are being washed from the salts by condensate running down the annulus side. It is possible that complex salts such as magnesium oxychlorides are precipitated within the flue so that the chloride does not permeate.

The mortar samples were also analyzed by X-ray diffraction and α quartz (SiO_2) from the aggregate was the predominant compound identified. Low levels of gypsum were found in mortar samples taken from the annulus side, but this does not appear to be detrimental. Elpasolite (K_2NaAlF_6) was found in one annulus mortar sample, apparently formed by crystallization from the permeating condensate. The molar ratio of potassium to sodium in elpasolite is higher than in the condensate analysis, suggesting that some potassium may have leached from the mortar itself. However, this mortar sample appeared to be sound.

Brick samples were drilled only from the inside of the flue. The only compounds identified by X-ray diffraction were quartz, hematite (Fe_2O_3), and mullite ($3Al_2O_3 \cdot 2SiO_2$), all of which would be expected in red shale brick. Because the bricks were dense, showed no signs of problems, and showed no evidence of detrimental phases at the inner face of the flue, no further analyses were conducted on them.

As a result of this investigation, it can be concluded that there does not appear to be noticeable deterioration of the mortar or the bricks at the base of the stack, both on the inside and annulus side of the flue. Annulus pressurization has not prevented condensate permeation through the flue, but may have slowed it slightly. Calcium and magnesium sulfate salt deposits which form in the annulus are due to permeation of the stack condensate through the flue and crystallization on the exterior surface. The salts themselves are not a major problem, but the condensate from which they form is acidic, high in fluorides, and corrosive to the reinforcing bands. Although fluorides were present in the condensate, a complex alkali aluminum fluoride salt was detected only in one mortar sample. Chlorides were present in the condensate, but were not detected in the salts in the annulus, in aqueous leachings from the salts, or within the mortar.

DISCUSSION

Obviously, the performance of an outlet duct or stack lining depends upon the environmental conditions to which it is exposed. It appears that the most severe conditions occur when wet scrubbed gas is mixed with hot bypassed gas or when a duct segment is alternately exposed to wet gas and hot gas. The sulfur, fluorine, and chlorine content of the coal may also be important factors, as well as the hot gas/wet gas ratio in the case of mixing. Also, the concentration of soluble species such as chlorides in the duct or stack condensate is affected by carry-over of scrubbing liquor from the mist eliminator. The concentration of these species in the scrubbing liquor is, in turn, affected by the overall water balance for the FGD system, i.e., open-loop versus closed-loop operation. It is difficult to recommend a preferred material for the most severe conditions. With regard to stacks, acid-resistant brick and mortar is the only material in service for wet gas/hot gas conditions, but leaning of free-standing brick flues has occurred in several cases. Additional research is needed to identify the causes of the leaning phenomenon, and research should continue on the performance of materials in various environments (temperature, acidity, chlorides, fluorides, substrate geometry, ambient conditions, etc.).

The utility industry should recognize that characterization and, to some extent, control of the outlet duct and stack environment are important even for FGD systems which are operating satisfactorily. This information, if available, could be useful in identifying stations with similar environments which may have materials problems and/or solutions for them. Consequently, even though a utility appears to be obtaining good performance from an outlet duct and/or stack, occasional characterization of the condensate (especially pH and fluoride, chloride, and sulfate concentrations) would be desirable. This information would be especially helpful in the event a problem were to develop in the future.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

REFERENCES

1. Rosenberg, H. S., et al. Construction materials for wet scrubbers. EPRI CS-1736, Electric Power Research Institute, Palo Alto, California, 1981.

2. Rosenberg, H. S., et al. Construction materials for wet scrubbers: update. EPRI CS-3350, Electric Power Research Institute, Palo Alto, California, 1984.

3. Dille, E. R. and Martin, P. E. Stack liners and stack corrosion in wet scrubber systems. Paper presented at 43rd Annual Meeting of the American Power Conference, Chicago, Illinois. April 27-29, 1981.

4. Rosenberg, H. S., et al. Operating experience and performance analysis of materials for stacks of wet flue gas scrubbers. In: Proceedings of the 1984 Air Pollution Seminar. National Association of Corrosion Engineers, Houston, Texas, 1984. p. 1/1.

5. Harada, Z. and Goto, M. On the synthesis of jarosite. J. Mineralogy (Japan). 1:344, 1954.

6. Koch, G. H., et al. Materials evaluation in the mixing zone of R. D. Morrow, Sr. Generating Station. Report to be published, Electric Power Research Institute, Palo Alto, California.

7. Koch, G. H. Alloy evaluation in the outlet duct of Duck Creek Station. Report to be published, Electric Power Research Institute, Palo Alto, California.

8. Martin, W. C., et al. Acid deposition on ductwork. EPRI CS-3240, Electric Power Research Institute, Palo Alto, California, 1983.

LEANING BRICK CHIMNEY LINERS AT COAL FIRED POWER PLANTS

by: E. R. Dille
Chemical Engineering Consultant
Burns & McDonnell
P.O. Box 173
Kansas City MO 64141

D. L. Krueger
Chemical Engineering Consultant

R. G. Rhudy
Project Manager
EPRI
P.O. Box 10412
Palo Alto CA 94303

INTRODUCTION

Leaning brick liners in stacks downstream of wet flue gas desulfurization (FGD) systems are a serious problem that has recently surfaced in the utility industry. While the information available suggests that so far the problem affects only a small number of stacks (11), the modifications necessary to repair or replace an existing stack liner represent a major investment. To date, little information has been available to determine the nature and extent of the problem. Accordingly, the Electric Power Research Institute (EPRI) has initiated a project to evaluate the severity of the problem, identify the cause or causes, and develop preventative measures. This paper documents the currently known information on leaning stacks, including what is known concerning the magnitude and cause of the problem.

STACK DESIGN INFORMATION

The FGD brick stack liner installations represent a variety of service conditions, designs, and materials of construction as shown in Table 1.

Generally, the service conditions are defined by the percent sulfur in the coal, the amount or frequency of bypass gas flow, and the presence or absence of reheat. Typical system configurations are shown in Table 2, along with an indication of which stacks are leaning. If the system is like configuration (1) in Table 2, stack temperatures are generally 150 degrees to 190 degrees F depending on the amount of reheat. For configuration (4), the flue gases are saturated with moisture and range from about 115 degrees to 135 degrees F. These conditions remain relatively constant during operation for both configuration (1) and (4). For the other two configurations, the conditions in the stack can experience significant fluctuations depending on the frequency and amount of bypass or reheat required. The amount of bypass or reheat is controlled by factors such as coal sulfur level and SO_2 removal requirements, boiler load, the number of modules in operation, and the amount of reheat desired. Conditions can range from scrubbed, 115 degrees to 135 degrees F saturated gas, to 170 degrees to 320 degrees F unscrubbed gas.

TABLE 1. WET FGD SYSTEMS WITH BRICK FLUES

Utility & Plant	Sulfur in Coal (wt%)	Type of FGD System	Start Up Date	Stack Height (ft)[a]	Reheat Type[b]	Pressurized Annulus	Type of Bricks: Clay Type	Type of Bricks: ASTM C279 Absorption	Type of Mortar
Cooperative Power Association									
Coal Creek 1	0.63	Lime/Fly Ash	5/79	650	BPD	Yes	Red Shale	Type H	Sauereisen No. 65
Coal Creek 2	0.63	Lime/Fly Ash	6/80	650	BPD	Yes	Red Shale	Type H	Sauereisen No. 65
Minnesota Power & Light									
Clay Boswell 4	0.94	Lime/Fly Ash	3/80	600	BPD	Yes	Fireclay	Type H	Corlok B
Cincinnati Gas & Electric									
East Bend 2[c]	3.7	Lime	3/81	650	BPD	Yes	Fireclay	Type H	Corlok B
Colorado-Ute Electric									
Craig 1	0.45	Limestone	10/80	600	BPD	Yes	Fireclay	Type H	Corlok B
Craig 2	0.45	Limestone	12/79	600	BPD	Yes	Fireclay	Type H	Corlok B
South Mississippi Electric Power									
R. D. Morrow 1	1.1	Limestone	9/78	400	BPD	No(Possible)	Red Shale	—	Sauereisen No. 65
R. D. Morrow 2	1.1	Limestone	6/79	400	BPD	No(Possible)	Red Shale	—	Sauereisen No. 65
Texas Utilities									
Martin Lake 1	0.7-1.5	Limestone	4/77	450	BPD	No	Unknown	Unknown	Corlok B
Martin Lake 2	0.7-1.5	Limestone	5/78	450	BPD	No	Unknown	Unknown	Corlok B
Martin Lake 3	0.7-1.5	Limestone	2/79	450	BPD	No	Unknown	Unknown	Corlok B
Monongahela Power									
Pleasants	3.0	Lime	1/81	1,000	BPD	Yes	Fireclay	Type H	Sauereisen No. 65
Kansas Power & Light									
Jeffrey 1	0.32	Limestone	8/78	600	BPD	Yes	Red Shale	Type H	Corlok B
Jeffrey 2	0.32	Limestone	1/80	600	BPD	Yes	Red Shale	Type H	Corlok B
Jeffrey 3[c]	0.32	Limestone	3/83	600	BPD	Yes	—	—	—
Utah Power & Light									
Hunter 1	0.55	Lime	5/79	600	BPD	No(Possible)	—	Type H	Corlok B
Hunter 2	0.55	Lime	6/90	600	BPD	No(Possible)	—	—	Corlok B
Hunter 3[c]	0.55	Lime	4/81	—	—	—	Red Shale	Type H	Sauereisen No. 65
Huntington 1	0.43	Lime	5/78	600	IND	Yes	Red Shale	Type H	Corlok B
Public Service Co. of New Mexico									
San Juan 1	0.8	Wellman-Lord	4/78	400	IND	No	Red Shale	Type H	Corlok B
San Juan 2	0.8	Wellman-Lord	9/78	400	IND	No	Red Shale	Type H	Uncertain
San Juan 3[c]	0.8	Wellman-Lord	1/80	400	IND	No	Unknown	—	Corlok B
San Juan 4[c]	0.8	Wellman-Lord	3/82	400	IND	No	Unknown	—	Corlok B
Nevada Power Company									
Reid Gardner 1	0.6	Soda Ash	3/74	200	IND	Yes	Unknown	—	Sauereisen
Reid Gardner 2	0.6	Soda Ash	4/74	200	IND	Yes	Unknown	—	Not acid-resistant (gunited)
Reid Gardner 3	0.6	Soda Ash	7/76	200	IND	Yes	Unknown	—	Sauereisen No. 65
Reid Gardner 4[c]	0.75	Soda Ash	6/83	500	—	—	Unknown	—	Sauereisen No. 65
Houston Lighting and Power									
W. A. Parish 8[c]	0.5	Limestone	10/82	500	BPD	—	Unknown	—	Corlok B
San Miguel Electric Cooperative									
San Miguel 1[c]	1.8	Limestone	8/81	447	IND	—	Unknown	Type H	—

[a] *One ft=0.3048 m*

[b] *Abbreviations used are*
BPD=Bypass to duct
BPS=Bypass to stack
IND=Indirect

[c] *Not included in Table 1*

TABLE 1. CONTINUED

							Type of Bricks		
Utility & Plant	Sulfur in Coal (wt%)	Type of FGD System	Start-Up Date	Stack Height (ft)[a]	Reheat Type[b]	Pressurized Annulus	Clay Type	ASTM C279 Absorption	Type of Mortar
Alabama Electric Cooperative									
Tombigbee 2	1.6	Limestone	9/78	400	BPD	Yes	Fireclay	Type H	Sauereisen No. 65[c]
Tombigbee 3	1.6	Limestone	6/79	400	BPD	Yes	Fireclay	Type H	Sauereisen No. 65[c]
Associated Electric Cooperative									
Thomas Hill 3[d]	4.8	Limestone	10/82	620	None (BPS)	Yes	Red Shale	7%	Sauereisen No. 65
Southern Illinois Power Cooperative									
Marion 4	3.5	Limestone	5/79	400	None (BPS)	Yes	Red Shale	Type H	Corlok B
Southern Indiana Gas & Electric									
A. B. Brown 1	3.6	Double Alkali	4/79	497	None (BPS)	Yes	Red Shale	Type H	Corlok B
Springfield City Utilities									
Southwest 1	2.5-4.5	Limestone	4/77	385	None (BPS)	No	Red Shale	Type H	Corlok B
(Southwest 1 reline)			(5/83)	(385)	(None)(BPS)	(Yes)	(Fireclay)	(2-4%)	(Sauereisen No. 65)
Springfield Water, Light & Power									
Dallman 3	2.5-4.0	Limestone	10/80	500	BPS	No	Red Shale	Type H	Corlok B
Arizona Public Service									
Four Corners 1 and 2	0.75	Lime/Fly Ash	11/79	250	None	Yes	Red Shale	Type H	Corlok B
Four Corners 3	0.75	Lime/Fly Ash	11/79	250	None	Yes	Red Shale	Type H	Corlok B
Commonwealth Edison									
Powerton 51[e]	3.6	Limestone	6/80	450	IND	Yes	—	Type L	—
Duquesne Light									
Phillips	2.3	Lime	7/23	340	None	Yes(1983)	Red Shale	Type L	Sauereisen No. 65
Elrama	2.0	Lime	10/75	400	None	No	Red Shale	Type L	Sauereisen No. 65
Pacific Power & Light									
Jim Bridger 4	0.6	Soda Ash	9/79	500	None (BPD)	Yes	Fireclay	Type H	Corlok B
Columbus & Southern Ohio Electric									
Conesville 5 and 6	4.5	Lime	3/78	800	None (BPD)	Yes	Red Shale	—	Sauereisen No. 65
West Penn Power									
Mitchell 3[d]	2.8	Lime	9/82	400	—	No	Fireclay	Type H	Sauereisen No. 65
Texas Utilities									
Monticello 3	0.5	Limestone	7/78	600	BPD	No	Unknown	Unknown	Corlok B
Basin Electric Power Cooperative									
Laramie River 1	0.35	Limestone	7/81	600	BPS	Yes	Two Types[f]	Two Types[f]	Sauereisen No. 65
Laramie River 2	0.35	Limestone	7/81	600	BPS	Yes	Red Shale	Type H	Sauereisen No. 65
Utah Power and Light									
Naughton 3[d]	0.5	Soda Ash	1/83	400	BPD	Yes	—	—	Sauereisen No. 65

[a] *One ft=0.3048 m*

[b] *Abbreviations used are*
BPD=Bypass to duct
BPS=Bypass to stack
IND=Indirect

[c] *Sauereisen No. 33 in top 25 ft (7.6 m) above rain cap*

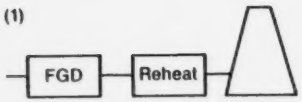
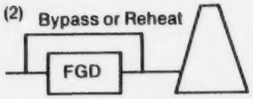
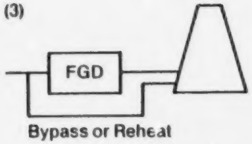
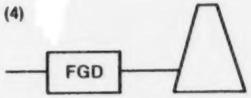
[d] *Not included in Table 1*

[e] *Scrubber operated only a few months during 1980, utility went to low sulfur coal*

[f] *Shale in lower 100 ft (30 m), fireclay in top 500 ft (150m)*

Reproduced from
best available copy.

TABLE 2. SYSTEM CONFIGURATION

(1) 	HS	Powerton 51 Widows Creek 8 San Miguel 1
	LS	Cholla 1 Will County 1 Hunter 1, 2, 3 Huntington 1 Reid Gardner 1, 2, 3, 4 San Juan 1, 2, 3, 4
(2) 	HS - Reheat	Tombigbee 2, 3, ▲ Pleasants 2 East Bend 2 Gibson 1 △
	Bypass	Conesville 5, 6
	LS - Reheat	Craig 1, 2 Coal Creek 1, 2 ▲ Jeffrey 1, 2, 3 ▲ Clay Boswell 4 R.D. Morrow 1, 2 Martin Lake 1, 2, 3 Monticello 3 Naughton 3 Parish 8 Four Corners 1, 2, 3, 4, 5
	LS - Bypass	None
(3) 	HS - Reheat	Dallman 33 △ A.B. Brown 1 △
	HS - Bypass	Marion 4 △ Southwest 1 △
	LS - Reheat	Laramie 1, 2 ▲
(4) 	HS	Elrama Phillips

△ *Major Lean Reported*
▲ *Minor Lean Reported*

Fluctuations can cycle over periods as short as 1 hour to daily. Maintenance requirements or emergencies can result in infrequent but significant fluctuations in service conditions.

Design of a typical dual entry stack is shown in Figure 1. Generally, the flues in brick stacks are made of red shale or fireclay acid-resistant brick with a potassium silicate mortar. In about half of the cases, the annular space between the shell and the liner is pressurized to prevent flue gas leakage into the annulars. This pressurization may also retard liquid migration through the liners, but it does not stop it completely. Evidence is available indicating that chrystalization does indeed occur on the outside of the stack.

EXTENT OF THE PROBLEM

In the utility industry, for units greater than 200 MW, there are slightly more than 200 brick-lined stacks. Approximately 50 of these are associated with wet FGD systems. Of these 50 stacks, 6, or 12 percent, are known to have significant leaning problems and several others to have a lesser degree of lean. Data on the extent of the problem for the leaning stacks is shown in Table 3. The first six units listed in Table 3 have a serious leaning problem with measured leans ranging from 18 to 27 inches. Four of the serious leaning liners have leaned in the direction of the breechings. The remaining two serious leaning liners have spiraled away from the breechings. Two of these units, Southwest 1 and A. B. Brown 1, have instituted major modifications to eliminate the problem. At the Southwest station, the stack liner was removed and rebuilt in 1983 using fireclay bricks and mortar from a different supplier, plus the addition of a pressurized annulus. At A. B. Brown 1, a separate brick liner was built inside the existing liner for the bottom 170 feet of the stack. A simplified drawing for the A. B. Brown 1 modification is shown in Figure 2.

The other units listed in Table 3 lean to a much lesser extent, although the service times are similar to the more severely leaning stacks. This may mean that a different mechanism is causing the lean at these sites, or that a less severe version of the same mechanism is the casual factor.

One additional point of interest is that discussions with stack erectors indicate that a 1 inch per 100 feet of stack height lean is not unusual in a new stack. This is a similar value to the lean in the less severe leaning stacks. Therefore, unless evidence of movement exists (e.g., cap deformation), this amount of liner lean may be normal.

DISCUSSION

During operation, the stack lining may experience temperature fluctuations from 115 degrees to 350 degrees F, and for short periods, up to 600 degrees F. Acid (H_2SO_4, HCl, HF) deposition can occur, or moisture deposition or condensation can occur, if the gas or wall temperature is low enough, followed by acid absorption. Slurry droplets not removed in the mist elimination system can impact, evaporate, and build up solids layers on the surface of the brick. The composition of the slurry droplets is determined mainly by the type of FGD system and the source of the liquid used for mist eliminator washing. Clearly the brick lining can see a wide range of service conditions.

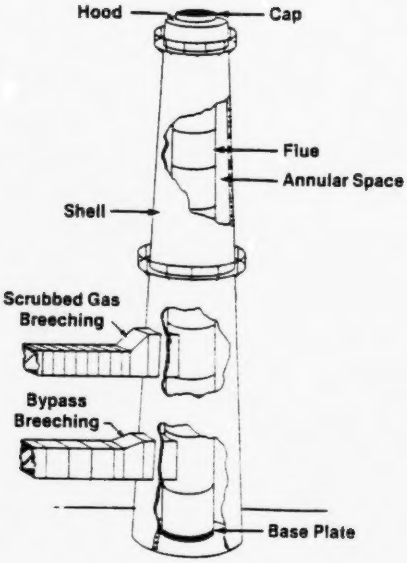

Hood
Cap
Flue
Annular Space
Shell
Scrubbed Gas Breeching
Bypass Breeching
Base Plate

FIGURE 1. A TYPICAL STACK

TABLE 3. LEANING BRICK STACKS

Station	Utility	Start Date	Service Time, Yr.	Amount of Lean, in.	Direction of Lean
1. A.B. Brown 1	So. Indiana Gas and Electric	4/79	6	18	Spiral, away from Breeching
2. Dallman 33	Springfield WL&P	10/80	4½	19	Toward Breeching
3. Gibson 1	P.S. of Indiana	10/82	2½	20	Toward Breeching
4. Thomas Hill 3	Assoc. Elec. Coop.	10/82	1, 2½	10, 24	Toward Breeching
5. Marion 4	So. Illinois Power Coop.	4/79	6	24	Toward Breeching
6. Southwest 1	City Utilities of Springfield	4/77	6	27	Spiral away from Breeching
7. Coal Creek 1	Coop. Power Assoc.	5/79	6	6	
2		5/80	5		
8. Jeffrey 1	Kansas Power & Light	8/78	6½	6	
9. Laramie 2	Basin Elect. Power Coop.	7/81	4	<6	
10. Tombigbee 2(1)	Alabama Elec. Coop	9/78	6½	4	Toward Breeching
3(1)		9/79	5½	4	Toward Breeching

(1) Two Flues in One Shell

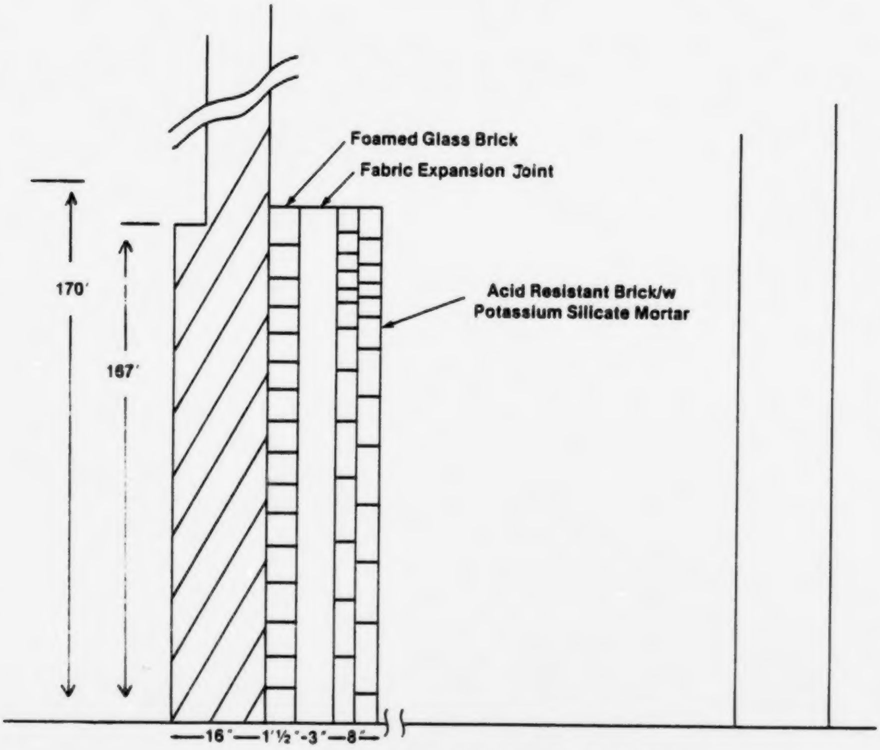

Foamed Glass Brick
Fabric Expansion Joint
Acid Resistant Brick/w Potassium Silicate Mortar
170'
167'
16"
1'½"
3"
8"

FIGURE 2. A.B. BROWN STATION
STACK REPAIRS

As reported by others(1), most of the known leaning stacks seem to be associated with conditions where bypass or reheat is mixed with scrubbed gas in the stack. Also, most of the stacks with a minor leaning problem are associated with mixing of reheat and scrubbed gas in the ductwork upstream of the stack.

All of the stacks with major leaning problems are constructed of red shale, acid-resistant bricks, Type H, with potassium silicate mortar.

Four of the major leaning stacks have experienced significant buildup of solids in the ductwork leading to the stack and on the stack lining. At the Thomas Hill 3 station, solids obtained in scale from the stack were analyzed. Results are presented in Table 4.

Although the data show wide ranges, the material appears to be mainly sulfate compounds of calcium and magnesium with small amounts of iron and aluminum. All of these compounds represent potential irreversible growth compounds. An irreversible growth compound can cause internal stresses and irreversible growth in the brick or mortar by expansion due to chemical reaction or hydration. An illustration of this process for sulfate compound hydration is shown in Figure 3.

For calcium compounds, the anhydrite is favored above 212 degrees F and for the magnesium compounds, $MgSO_4.H_2O$ is the stable compound 158 degrees F to 220 degrees F. $MgSO_4 \cdot 6H_2O$ is the stable compound between 120 degrees F and 158 degrees F. Penetration of these compounds into the brick is confirmed by the sample taken from the brick surface in the annular space between the liner and the shell.

Core samples were also obtained from various locations in the Thomas Hill 3 stack liner and analyzed for thermal expansion coefficient, total sulfate, and compound identification by x-ray diffraction. The core locations are shown in Figure 4, and the analyses results in Table 5.

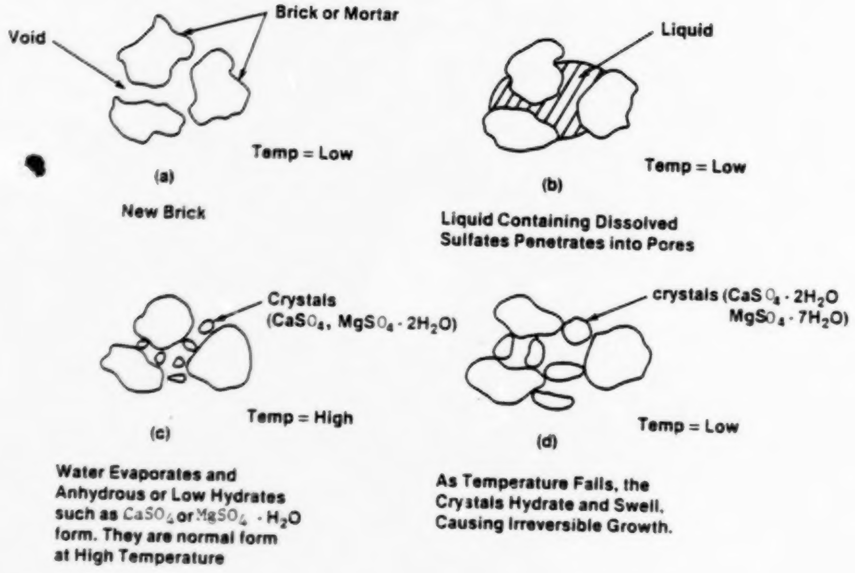
From analysis of the results, it is clear that sulfate in the form of magnesium and calcium compounds has penetrated the brick and mortar - especially the mortar. Also, since the highest penetration has occurred opposite the scrubber breeching, there appears to be a relationship between what is carried in the flue gas that can impact and be deposited on the lining surface (i.e., condensed sulfuric acid, fly ash or scrubber carryover), and increased penetration of the lining. The fact that most of the compounds are calcium and magnesium based suggest scrubber carryover since this system is a magnesium promoted limestone wet scrubber, and the slurry contains high levels of these elements. The identification of potassium sodium sulfate on the cold face of locations A and D indicate that in addition to the compounds mentioned previously, sulfuric acid penetrated the lining and reacted with mortar materials to form these compounds.

THEORY FOR STACK LEAN

While admittedly the currently available information on leaning stacks is extremely limited, the data do provide enough information to propose an explanation for the phenomenon. It appears that a number of conditions may be

TABLE 4. ANALYSIS OF STACK SOLIDS BUILDUP

Compound	Amount, Wt.%				
	Floor	Wall	• Wall	Stack Emission	Annulus
$MgSO_4 \cdot 6H_2O$		22	8	15	54
$MgSO_4 \cdot H_2O$	52	16		5	16
$CaSO_2 \cdot 2H_2O$		5	11		18
$CaSO_2$	5	54	80	72	5
$FeSO_4\ 4H_2O$			4		
$Al_2(SO_4)_3 \cdot xH_2O$	4				


Void
Brick or Mortar
Temp = Low
(a)
Liquid
Temp = Low
(b)
Crystals ($CaSO_4$, $MgSO_4 \cdot 2H_2O$)
Temp = High
(c)
crystals ($CaSO_4 \cdot 2H_2O$ $MgSO_4 \cdot 7H_2O$)
Temp = Low
(d)

New Brick

Liquid Containing Dissolved Sulfates Penetrates into Pores

Water Evaporates and Anhydrous or Low Hydrates such as $CaSO_4$ or $MgSO_4 \cdot H_2O$ form. They are normal form at High Temperature

As Temperature Falls, the Crystals Hydrate and Swell, Causing Irreversible Growth.

FIGURE 3. PATTERN FOR IRREVERSABLE SALT GROWTH

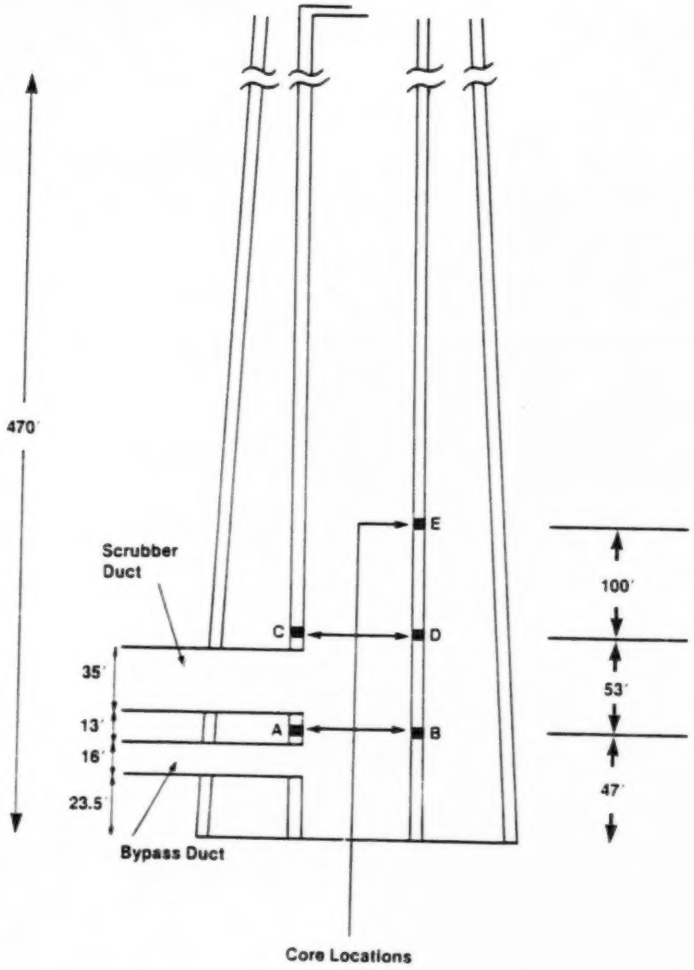

470′
Scrubber Duct
Bypass Duct
35′
13′
16′
23.5′
A
B
C
D
E
100′
53′
47′
Core Locations

FIGURE 4. THOMAS HILL
STACK CORE LOCATIONS

TABLE 5. THOMAS HILL 3
CORE ANALYSIS

Location	Thermal Expansion Coefficient (10^{-6})	Total Sulfate, Wt. %		X-Ray Diffraction Trace Compounds	
		Brick	Mortar	Hot Face	Cold Face
A. Between Bypass and FGD Duct on Breeching Side of Liner	6.9	1.41	3.87	$MgSO_4 \cdot 6H_2O$ $CaSO_4$	NaF K_2SiF_6 $K_3Na(SO_4)_2$
B. Same as A but on Side Away from Breeching	8.0	1.29	12.20	$MgSO_4 \cdot H_2O$ $MgSO_4 \cdot 6H_2O$ $CaSO_4$	NaF
C. Above FGD Duct Entrance on Breeching Side of Liner	6.9	—	—	$MgSO_4 \cdot 6H_2O$ $CaSO_4$ $K_3Na(SO_4)_2$	NaF K_2SiF_6
D. Same as C but on Side Away from Breeching	8.1 8.5	1.18	2.29	$MgSO_4 \cdot 6H_2O$ $K_3Na(SO_4)_2$	NaF K_2SiF_6 $K_3Na(SO_4)_2$
E. 100 Feet Above FGD Duct Breeching on Side away from Breeching	6.6	0.61	1.81	$CaSO_4$	NaF
F. New Brick (from Orginal Supply)	8.1	0.11	0.1	NaF K_2SiF_6	—

necessary to cause liner lean, but that none are necessarily sufficient by themselves to result in a major lean problem. Basically, the concept is that condensed sulfuric acid and scrubber slurry get carried into the stack and deposit on the liner - especially opposite the breeching. The liquid phases penetrate the brick and/or mortar, and either chemically react (e.g., sulfuric acid forming potasium sodium sulfate) and cause expansion, or precipitate (e.g., formation of $MgSO_4 \cdot H_2O$) during high temperature episodes when the flue gas impinging on the walls is from bypass and, when the affected area cools, some of the salts can hydrate, swell, and cause expansion. If this process occurs on the side opposite the stack breeching, the result will be a lean toward the breeching. Most sites have experienced this type of lean.

These conditions would be most likely to occur for configuration (3) in Table 2 where bypass exists and is mixed in the stack (providing high probability of temperature fluctuations and the presence of sulfuric acid), and slurry carryover from the scrubber is a problem (as indicated at several of these sites). The configuration (2) sites would be better, but still potential leaners, depending on how the quality of gas mixing in the duct reduces the temperature gradients experienced in the stack. For configurations (1) and (4), thermal gradients in the stack would not be expected. Factors such as the amount of slurry carryover or the amount of acid present may also affect the severity of the lean.

CONCLUSION

While the data may be sufficient to propose a mechanism for causing stack liners to lean, a great deal of work needs to be done before the cause of stack lean can be confirmed. The work EPRI has initiated should aid in resolving the issue. It is clear however, that consideration will have to be given to this problem when designing new systems, and a close watch will need to be kept on stacks that may be at risk of leaning.

New designs may require configuration changes or even changes in materials of construction. While the problem may not be major for the utility industry when compared to the number of existing units, it is an important problem that needs resolution.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and, therefore, the contents do not necessarily reflect the views of the agency and no official endorsement should be inferred.

BIBLIOGRAPHY

1. "Operating Experience and Performance Analysis of Materials for Stacks of Wet Flue Gas Scrubbers," H.S. Rosenberg, Et.Al

THE ECONOMICS OF CLAD METALLIC FABRICATION VERSUS SOLID ALLOY METAL FABRICATION

by: E. H. Cloth
R. Kreider
Stone & Webster Engineering Corporation
Cherry Hill, New Jersey 08034

ABSTRACT

The purpose of this analysis of FGD materials is to provide economic guidance in the selection of a clad metallic fabrication system versus a solid metal fabrication. A simplified FGD tower shell was designed to provide a common basis for the costs.

The material and fabrication costs of solid alloys were compared with clad metal fabrications, i.e., roll-bonded, alloy lining, to determine the potential economical savings. Solid alloy materials costs spanned the $2.00 to $11.00 per pound range, which included 316L, an austenitic stainless steel, to C-276, a nickel base alloy. The costs included plate or sheet material costs, weld filler material costs, and welding man-hour costs. The investigation indicates possible savings for clad alloy fabrications over solid alloy fabrications when the solid alloy cost is in the $2.00 to $3.00 per pound range with savings approaching the potential of 30 to 60 percent in the higher-priced alloys such as 625 or C-276. The welding of thin alloy sheets, 1/16 inch and 1/8 inch thick, on a carbon steel shell can also become commercially advantageous in the higher-priced alloys.

INTRODUCTION

The corrosive environments and temperatures that are encountered in flue gas desulfurization (FGD) systems generally require more expensive metal alloys to provide the desired 30-year plant life with minimum maintenance and replacement costs. Clad metal fabrications, which replace a portion of the higher-cost alloy with the lower-priced carbon steel without sacrificing the corrosion resistance, are a means of reducing the material costs. It is also justifiable as a means of obtaining a better corrosion-resistance barrier (better alloy layer in the clad material) for costs similar to solid alloy fabrications. This paper is taken from a SWEC study funded by EPRI, T. M. Morosky, Project Manager, No. EPRI CS-3628, Project RP1871-8.

The potential savings in utilizing a clad alloy fabrication versus a solid alloy plate fabrication was determined. Guidelines are provided when alloy metal cladding systems should be considered for economic reasons. The investigation of clad metal systems included roll-bonded, explosive-bonded, and alloy lining (the welding of thin alloy sheets over a carbon steel shell). In addition, commercial availability of the materials was also addressed in the size ranges required. As a means of providing a common fabrication baseline, a simplified FGD tower shell was designed. It was used to compare the material and welding fabrication costs for the various solid alloy and clad alloy systems. Welding criteria were established to ensure the corrosion resistance of the weld joints, with specific emphasis on the clad metal welding.

APPROACH

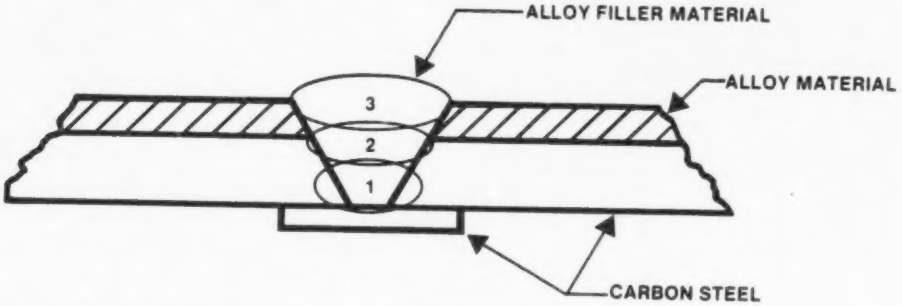
Alloys were selected on the basis of commercial availability and potential application to the FGD systems. Specific materials were chosen from each potential grouping that could be considered representative and also provide the desired material cost range for the investigation. Clad thicknesses of 1/16 inch and 1/8 inch were selected to provide sufficient alloy thickness for minor pitting corrosion. This assumes that the alloy that has been selected has sufficient corrosion resistance to prevent a pitting/crevice corrosion attack in its intended environment. The alloys used in the investigation are listed in Table 1. Clad alloy fabrication possibilities were investigated for all the alloys shown in Table 1.

TABLE 1. METAL ALLOYS INVESTIGATED

Alloy	Chemical Analysis Major Element (%)									
	C	Fe	Ni	Cr	Mo	Ti	Cu	Al	Co	W
316L	0.03	Rem.	10/14	16/18	2/3	-	-	-	-	-
904L	0.02	Rem.	23/28	19/23	4/5	-	1/2	-	-	-
G	0.05	18/21	54	21/23.5	5.5/7.5	-	1.5/2.5	-	(Cb&Ta) (1.75/2.50)	
625	0.10	5.0	Rem.	20/23	8/10.0	-	-		(Cb&Ta) (3.15/4.15)	
C-276	0.02	4/7	Rem.	14.5/16.5	15/17	-	-	-	2.5	3/4.5
Titanium, Grade 2	0.10	0.30	-	-	-	Rem.	(N-.03, H-.015, O-.25)			

The welding technique utilized in the cost analysis for clad materials was such that the first weld layer is finished in the carbon steel, the second weld layer finished above the carbon steel to alloy bond line, and the third weld layer becomes essentially an undiluted weld pass to provide a corrosion surface equivalent to the wrought plate material or undiluted weld metal. The welding process utilized in the cost analysis was shielded metal arc welding (SMAW) with 1/8-inch diameter electrodes. This method would be readily available for both shop and field welding. Titanium fabrications utilized gas metal arc welding (GMAW) with 0.045-inch diameter filler metal.

A simplified FGD tower was designed with weld joint details that can be expected to prevent degradation of the weld metal from dilution from carbon steel. Figure 1 shows the type of joint detail and weld bead placement necessary to provide a suitable dilution-free final weld surface.



Note: The weld bead layers are placed to allow the final weld bead layer to be essentially undiluted by carbon steel to ensure the corrosion resistance of the weld joint.

Figure 1. Clad alloy welding approach.

Figure 2 shows the tower design. The design was modified to take advantage of the maximum sizes available in alloy, clad, or carbon steel plate and sheet widths to reduce the number of weld joints and minimize fabrication costs.

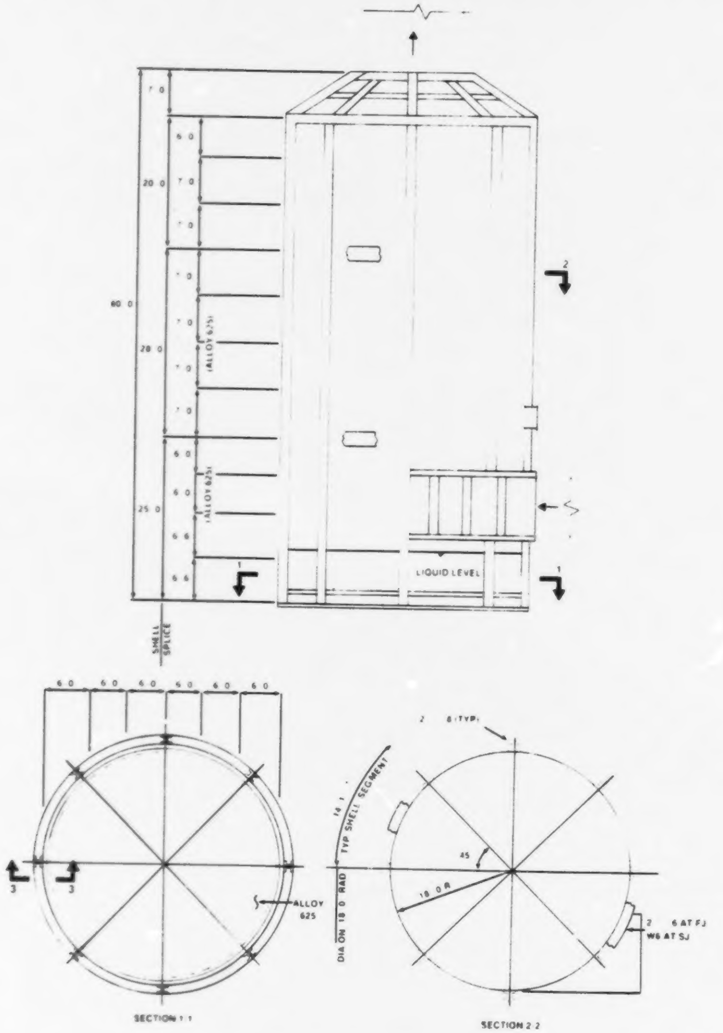

7 0
6 0
20 0
7 0
7 0
80 0
7 0
7 0
28 0
7 0
(ALLOY 625)
7 0
6 0
6 0
(ALLOY 625)
25 0
6 6
6 6
2
1
1
LIQUID LEVEL
SHELL
SPLICE
6 0
6 0
6 0
6 0
6 0
6 0
3
3
ALLOY
625
SECTION 1-1
2 8 (TYP)
14 1
TYP SHELL SEGMENT
DIA ON 18 0 RAD
45
18 0 R
2 6 AT FJ
W6 AT SJ
SECTION 2-2

Figure 2. Absorber tower.

Material costs and availability were obtained for the thickness range normally utilized in FGD designs. In addition, an assessment was made of the commercial availability of all the materials.

It is not the intent of this investigation to study every alloy but only to select representative materials from a cost standpoint. It is also recognized that fabrication costs can vary depending upon business conditions and an individual fabricator's or applicator's experience.

ANALYSIS

GENERAL

Solid alloy and clad alloy costs and potential availability, including maximum plate or sheet widths rolled in the mills, were determined. The clad metal information was obtained for 1/16-inch and 1/8-inch thick alloy on carbon steel plate in the total thickness range of 3/16 inch to 3/8 inch. The metal costs are listed in Table 2 and are presented as a single cost for the entire thickness range.

TABLE 2. METAL COSTS

(Material cost - $/lb)

Item	Thickness (in.)	316L	904L	Alloy G	625	C-276	Titanium	Carbon Steel
Plate	1/2	1.70	3.00	6.00	9.00	10.50	9.00	0.45
Sheet	1/16	-	4.20	7.00	10.20	11.50	8.80	
Sheet	1/8	-	4.00	6.80	10.00	11.25	8.50	
Clad*	1/16	1.50	2.80	3.80	4.50	6.00	-	
Clad*	1/8	1.80	3.00	4.30	5.50	7.00 (est.)	-	

*The availability of all the alloys as roll-bonded clad products remains to be accomplished, i.e., C-276; however, the commercial products are considered technically feasible by the mills.

Mill roll-bonded alloys are potentially available in thicknesses of 3/16 to 3/8 inch for all alloys, except titanium. There is, however, limited mill production on all the alloys, except 316L stainless steel and possibly alloy 625. Explosive bonded clad systems are available in thicknesses of 1/2 inch and greater and as a result were not included in this study. Alloy lining a cladding system that utilizes thin sheets of alloy materials welded to a carbon steel shell, also was investigated. Titanium, which is not welded to carbon steel, utilized sheets bolted to a carbon steel shell and subsequent welding of the titanium to itself to obtain the wallpapering effect.

COST ESTIMATING

The fabrication costs for the tower were estimated using published criteria and other cost-estimating practices. In all cases, a conservative approach to welding was utilized to provide maximum corrosion resistance in the weld joints using stringer bead techniques where possible and additional weld bead layers to result in undiluted weld metal on the process side in clad alloy fabrications. Designs for a basic tower shell were changed only to accommodate the availability of wider plate widths on certain materials, e.g., 120-inch clad materials versus 72-inch alloy plate widths. This allows a reduction in the number of horizontal weld joints necessary for a clad material fabrication with a potential reduction in welding costs. Appendix A provides the technique used to determine the fabrication costs together with examples of the cost estimating details for the tower solid alloys, and clad roll-bonded alloys. A composite summary of the solid alloy fabrications, the roll-bonded alloy clad fabrications, and the alloy lining fabrications are shown in Table 3.

TABLE 3. TOWER ALLOY COST SUMMARY

		Solid Plate Installed Shell Cost ($)					Roll-Bonded Clad Plate Installed Shell Cost ($)					Alloy Lining Installed Shell Cost ($)				
Material	Cost ($/lb)	Thickness (in.)	Plate	Filler Metal	Welding Time	Total	Thickness (in.)*	Plate	Filler Metal	Welding Time	Total	Thickness (in.)†	Plate	Filler Metal	Welding Time	Total
316L	1.70	1/4	188,000	7,000	36,000	231,000	1/16	163,000	16,000	31,000	210,000					
							1/8	197,000	16,000	31,000	244,000					
		3/8	282,000	9,000	49,000	340,000	1/16	244,000	25,000	64,000	333,000					
							1/8	294,000	25,000	64,000	383,000					
904L	3.00	1/4	332,000	17,000	36,000	385,000	1/16	305,000	16,000	31,000	352,000	1/16	159,000	32,000	99,000	290,000
							1/8	328,000	16,000	31,000	375,000	1/8	264,000	32,000	99,000	395,000
		3/8	497,000	23,000	49,000	569,000	1/16	456,000	25,000	64,000	545,000					
							1/8	489,000	25,000	64,000	578,000					
G	6.00	1/4	686,000	17,000	42,000	745,000	1/16	417,000	16,000	31,000	464,000	1/16	243,000	32,000	99,000	374,000
							1/8	478,000	16,000	31,000	525,000	1/8	432,000	32,000	99,000	563,000
		3/8	1,028,000	23,000	57,000	1,108,000	1/16	621,000	25,000	64,000	710,000					
							1/8	710,000	25,000	64,000	799,000					
Titanium, Grade 2	9.00	1/4	556,000	6,000	33,000	595,000	-	-	-	-	-	1/16	179,000	3,000	46,000	228,000
			-	-	-	-	-	-	-	-	-	1/8	306,000	3,000	46,000	355,000
		3/8	834,000	11,000	42,000	887,000	-	-	-	-	-					
625	9.00	1/4	1,028,000	17,000	42,000	1,087,000	1/16	494,000	16,000	31,000	541,000	1/16	334,000	32,000	99,000	465,000
							1/8	612,000	16,000	31,000	659,000	1/8	614,000	32,000	99,000	745,000
		3/8	1,542,000	23,000	57,000	1,622,000	1/16	736,000	25,000	64,000	825,000					
							1/8	908,000	25,000	64,000	997,000					
C-276	10.50	1/4	1,283,000	26,000	42,000	1,351,000	1/16	670,000	24,000	31,000	725,000	1/16	395,000	48,000	99,000	542,000
							1/8	807,000	24,000	31,000	862,000	1/8	731,000	48,000	99,000	878,000
		3/8	1,925,000	35,000	57,000	2,017,000	1/16	993,000	37,000	64,000	1,094,000					
							1/8	1,183,000	37,000	64,000	1,284,000					

*The clad thickness denotes the thickness of the alloy layer bonded to the carbon steel. The carbon steel thickness is increased to result in a total thickness equal to the solid alloy plate.

†The alloy lining sheet thickness that covers a 1/4-inch-thick carbon steel shell.

The material costs and man-hours are based on early 1985 data. The cost of materials was included without any overhead. The welding labor rate of $40/hr, includes fringe benefits and overhead and is considered a typical welding industry man-hour cost for the first half of 1985. All projected costs are in 1985 dollars.

DISCUSSION

The alloy fabrication study is an analysis of the cost-effectiveness of using clad alloy fabrication in comparison with solid alloy for the shell plate thickness ranges expected in FGD designs, 3/16 to 3/8 inch. It is not the intent of the analysis to indicate that an FGD tower or ductwork segment can be purchased for the costs indicated, but that the basic cost data would provide guidance to the industry when an alloy cladding system could be considered for potential cost savings. By restricting the costs to basic items, material costs (plate, sheet, and filler metal) and man-hour costs, the effect of the alloy plate cost becomes readily apparent on the total fabrication cost as it approaches $11 per pound.

The ability to realize cost savings with clad alloys is dependent upon the cost differential between the solid alloy and the clad alloy. The magnitude of the potential savings depends upon the cost of the solid alloys and the amount of alloy being replaced by relatively low-cost carbon steel. The investigation included 1/16- and 1/8-inch roll bond clad and 1/16- and 1/8-inch alloy sheets lined on a 1/4-inch carbon steel shell. For alloys such as 625 and C-276, which are in the $9 to $11 per pound range, substantial savings are possible when 25 to 50 percent of the alloy is being replaced by carbon steel at $0.45 per pound. Savings appear to be possible even when the alloy cost approaches $2 per pound, depending upon the thickness of the alloy layer. A comparison of the fabrication costs for the roll-bonded alloy clad and the alloy lining method with the solid alloy plate costs are shown in Table 4.

TABLE 4. TOWER COST COMPARISON - ALLOYS

			Fabrication Costs							
			Alloy Clad				Alloy Lining			
			1/8 in.		1/16 in.		1/8 in.		1/16 in.	
Material	Thickness (in.)	Solid Plate Cost ($)	Cost ($)	% Diff	Cost ($)	% Diff	Cost ($)	% Diff	Cost ($)	% Diff
316L	1/4	231,000	244,000	+6.0	210,000	-9.0				
	3/8	340,000	383,000	+13.0	333,000	-2.0				
904L	1/4	385,000	375,000	-3.0	352,000	-9.0	395,000	+3.0	290,000	-25.0
	3/8	569,000	578,000	+1.4	545,000	-4.4				
Alloy G	1/4	745,000	525,000	-30.0	464,000	-38.0	563,000	-24.0	374,000	-50.0
	3/8	1,108,000	799,000	-28.0	710,000	-36.0				
Titanium, Grade 2	1/4	595,000	-	-	-	-	355,000	-40.0	228,000	-62.0
	3/8	887,000								
625	1/4	1,087,000	659,000	-39.0	541,000	-50.0	745,000	-32.0	465,000	-57.0
	3/8	1,622,000	997,000	-39.0	825,000	-49.0				
C-276	1/4	1,351,000	862,000	-36.0	725,000	-46.0	878,000	-35.0	542,000	-60.0
	3/8	2,017,000	1,284,000	-36.0	1,094,000	-46.0				

The commercial availability of the roll-bonded alloy clad materials is considered possible, but overall mill experience is lacking except for 316L stainless steel and possibly Alloy 625. Alloy lining of thin alloy sheets on a carbon steel shell is also economical for such alloys as 625, C-276, etc, when roll-bonded metals are not available.

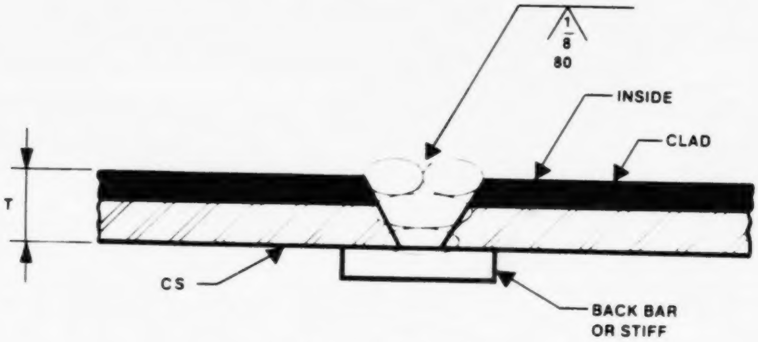
CONCLUSIONS AND RECOMMENDATIONS

The use of clad alloy fabrications as a cost reduction is possible as the solid alloy cost approaches the $2 to $3 per pound range in the FGD expected plate thickness range of 3/16 to 3/8 inch. The potential cost savings can approach the 30 to 60 percent range, with significant dollar savings for the alloys in the $9 to $11 per pound range, such as 625 and C-276. Such savings can be realized after taking additional steps in the welding to preserve the corrosion barrier.

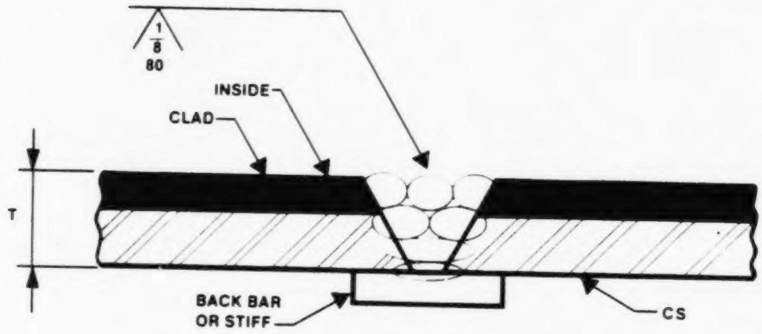
APPENDIX A PROCEDURE FOR DETERMINING WELDING FABRICATION COSTS

The welding fabrication costs were estimated using alloy manufacturers' guidelines and developed criteria to determine the amount of filler metal and man-hours required to weld with the SMAW (shielded metal arc welding) process, using a 1/8-inch diameter electrode. This process is considered the most readily available for both shop and field welding of stainless steel and nickel base alloys. The basic premise was to determine the number of weld bead lengths required for each weld joint, the amount of electrodes required, and the number of man-hours necessary to perform the welding. The GMAW (gas metal arc welding) process with 0.045-inch diameter wire was utilized for titanium welding. The stringer bead technique was factored into the costs. Also, additional weld beads were used in clad alloy fabrications when necessary to provide essentially a dilution-free weld layer on the process side.

The designs and weld joint details for the towers and ductwork are shown in Figures 1 and 2 and Figures A-1 and A-2. The number of weld beads for each weld joint are also shown in the weld joint details.

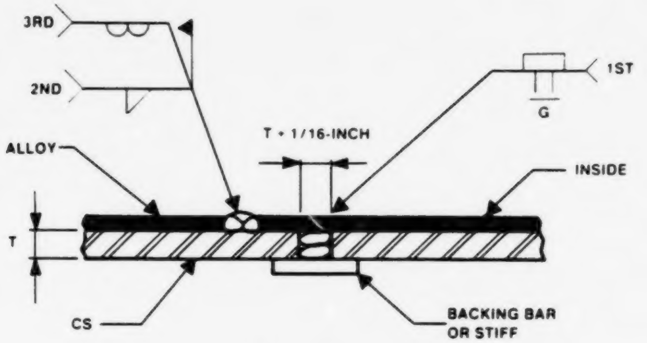


T = 3/16 INCH & 1/4 INCH

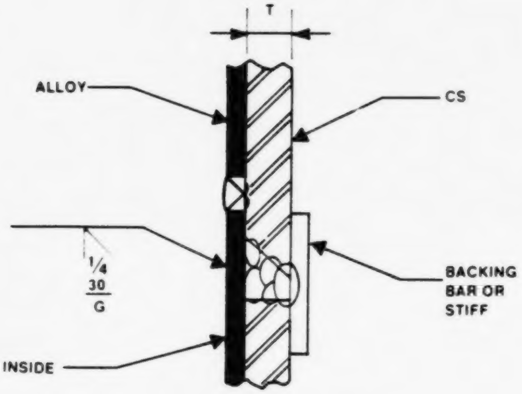


T = 5/16 INCH TO 3/8 INCH

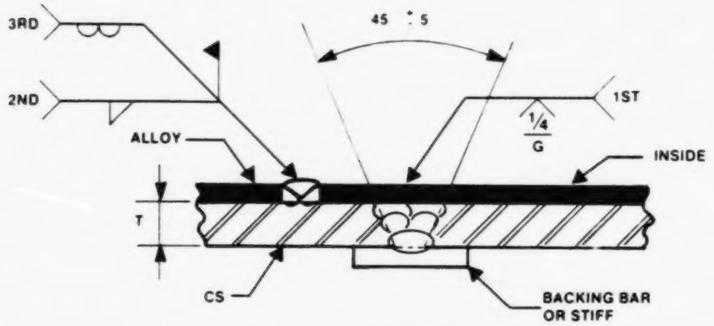
Figure A-1. Clad.


3RD
2ND
1ST
G
T + 1/16-INCH
ALLOY
INSIDE
T
CS
BACKING BAR OR STIFF

T = ¼-INCH AND UNDER


T
ALLOY
CS
¼
30
G
BACKING BAR OR STIFF
INSIDE

T = 5/16-INCH TO ⅜-INCH
HORIZONTAL POSITION


3RD
2ND
45 ± 5
1ST
¼
G
ALLOY
INSIDE
T
CS
BACKING BAR OR STIFF

T = 5/16-INCH TO ⅜-INCH
VERTICAL, FLAT POSITION

Figure A-2. Alloy lining.

The following criteria were used in calculating the amount of filler metal and welding man-hours required:

1. Amount of Filler Metal Required

   a. The number of weld beads for the joint was estimated.

   b. The total weld bead length was determined.

   c. The number of electrodes was determined assuming an SMAW process and a 1/8-inch diameter electrode that would deposit 5 inches of weld metal.

   d. The weight of required electrodes was determined by dividing Item C by the number of 1/8-inch diameter electrodes per 1 pound:

Electrode	No./lb
E7018	12.6
316L	13.8
625	16
C276	15

2. Number of Welding Man-hours Required

   a. Assume approximately 30 percent of an 8-hour shift is utilized in nonwelding tasks.

   b. Assume the burnoff time of a 1/8-inch, 12-inch long electrode is 1.25 minutes.

   c. The number of electrodes multiplied by the burnoff time provides the welding time.

   d. Allow approximately 1/2 minute per foot of weld bead for slag cleaning and 1/2 minute per electrode for wire changing and repositioning.

   e. The total welding time becomes the total of Items a through d.

   f. Multiply Item e by the following factors to obtain the welding man-hours:

Material	Factor
Carbon steel	1.0
Stainless steel	1.2
Nickel alloys	1.4
Clad materials	1.5
Titanium	2.0

The values used in determining the solid alloy tower costs and the 1/16-inch roll bonded clad costs are shown on Tables A-1 and A-2.

TABLE A-1. SOLID ALLOY AND CARBON STEEL - TOWER COST

Reproduced from
best available copy.

Material	Plate Thickness (in.)	Plate (lb)	$/lb	Plate Cost($)	Electrode	No. of Electrodes	No./lb	lb Electrodes	$/lb	Electrode Cost($)	Welding Hours	$/hr	Man-Hour Cost($)	Total Cost($)
C.S.	1/4	107,881	0.45	48,547	E7018	12,729	12.6	1,010.2	0.60	606	415	40	16,600	65,753
316L	1/4	110,433	1.70	187,736	316L	23,136	13.8	1,676.5	4.00	6,706	906	40	36,240	230,682
	3/8	165,650	1.70	281,605	316L	31,180	13.8	2,259.4	4.00	9,038	1,220.4	40	48,816	339,459
904L	1/4	110,433	3.00	331,299	625	23,136	16	1,446	12.00	17,352	906	40	36,240	384,891
	3/8	165,650	3.00	496,950	625	31,180	16	1,949	12.00	23,388	1,220.4	40	48,816	569,154
G	1/4	114,241	6.00	685,446	625	23,136	16	1,446	12.00	17,352	1,057	40	42,280	745,078
	3/8	171,362	6.00	1,028,172	625	31,180	16	1,949	12.00	23,388	1,424.8	40	56,992	1,108,552
625	1/4	114,241	9.00	1,028,169	625	23,136	16	1,446	12.00	17,352	1,057	40	42,280	1,087,801
	3/8	171,362	9.00	1,542,258	625	31,180	16	1,949	12.00	23,388	1,424.8	40	56,992	1,622,638
C276	1/4	122,238	10.50	1,283,499	C276	23,136	15	1,542.4	17.00	26,221	1,057	40	42,280	1,352,000
	3/8	183,358	10.50	1,925,259	C276	31,180	15	2,078.7	17.00	35,338	1,424.8	40	56,992	2,017,589

TABLE A-2. 1/16-INCH ROLL-BONDED ALLOY - TOWER COST

Material	Plate Thickness (in.)	Plate (lb)	$/lb	Plate Cost($)	Electrode	No. of Electrodes	No./lb	lb/Electrodes	$/lb	Electrode Cost($)	Welding Hours	$/hr	Man-Hour Cost($)	Total Cost($)
316L	1/4	108,773	1.50	163,160	625	21,542	16	1,346	12.00	16,152	785	40	31,400	210,712
	3/8	162,590	1.50	243,885	625	32,889	16	2,056	12.00	24,672	1,610	40	64,400	332,957
904L	1/4	108,773	2.80	304,564	625	21,542	16	1,346	12.00	16,152	785	40	31,400	352,116
	3/8	162,590	2.80	455,252	625	32,889	16	2,056	12.00	24,672	1,610	40	64,400	544,324
G	1/4	109,725	3.80	416,955	625	21,542	16	1,346	12.00	16,152	785	40	31,400	464,507
	3/8	163,542	3.80	621,460	625	32,889	16	2,056	12.00	24,672	1,610	40	64,400	710,532
625	1/4	109,725	4.50	493,763	625	21,542	16	1,346	12.00	16,152	785	40	31,400	541,315
	3/8	163,542	4.50	735,939	625	32,889	16	2,056	12.00	24,672	1,610	40	64,400	825,011
C276	1/4	111,724	6.00	670,344	C276	21,542	15	1,436	17.00	24,412	785	40	31,400	726,156
	3/8	165,541	6.00	993,246	C276	32,889	15	2,193	17.00	37,281	1,610	40	64,400	1,094,927

The work described in this paper was not funded by the U.S. Environmental Protection Agency, and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

Laboratory Evaluation as a Technique for Predicting the Behavior of Organic Coatings in FGD Systems

by: Malcolm L. White and Henry Leidheiser, Jr.
Center for Surface and Coatings Research
Lehigh University

G. H. Koch
Battelle Columbus Laboratories
505 King Avenue
Columbus, OH 43201-2693

ABSTRACT

A laboratory evaluation of several neat resin systems commonly used as the basis for formulated organic coatings in Flue Gas Desulfurization (FGD) systems was carried out by exposure of coated carbon steel substrates to dilute sulfuric acid at 60°C (140°F) for periods up to 3000 hours. Measurements of corrosion potential, AC conductance, tensile adhesion and weight gain revealed distinct differences in the behavior of the resin types in protection of the steel against corrosion. These results are compared with those obtained in an 18-month field study of formulated coatings (using the same resins as a base material) exposed to the extremely aggressive environment of the outlet mixing zone of the R.D. Morrow, Sr., FGD system. The correlations of resin/coating performance in the actual and simulated FGD environments were investigated with respect to both corrosion protection of the underlying steel and in the modes of failure for those materials that showed poor performance.

INTRODUCTION

With the increased use of FGD for removing acid components from coal combustion, there has been an attendant increase in the use of organic coatings for protection of the metallic materials of construction used in scrubber components where corrosion is a major problem. The prime objective of an FGD system is to remove SO_2 from the flue gas generated by coal combustion by counter current spraying with a lime or limestone slurry. The principal product of this reaction is calcium sulfite and sulfate. In an additional reaction, SO_2 reacts with water to form sulfurous and, on oxidation, sulfuric acids, which are extremely aggressive toward materials of construction. In addition to these aggressive constituents, the flue gas contains numerous trace elements which may have a beneficial or detrimental effect on materials of construction [1-3]. This highly acidic environment is particularly detrimental to cold-rolled carbon steel, which is a favored material of construction because of its relatively low cost.

Organic resin-based coatings are often used to protect carbon steel in FGD systems. These are generally formulated by mixing fillers, pigments, dispersing agents and other additives with common resin systems, such as epoxies, polyesters and vinyl esters, to increase their viscosities and to improve their thermal/mechanical characteristics. The formulated coating is then applied to the steel by spraying, troweling or roller coating. Following the cure of the two component systems, or evaporation of solvent used for application in the solvent-based systems, the coating system is ready for use.

A wide range of experiences with commercial coatings used in FGD systems has been reported [4]. Not only are there variations in the chemistry of the flue gas from station to station, but also different conditions in various parts of the system. For example, glass flake-filled polyester coatings have been reported to provide good protection for carbon steel at nine unspecified power plants constructed since 1972 [5]. However, at the Bruce Mansfield plant, Shippingport, PA, the same type of coating applied to chimney flues showed bubbling, softening and debonding when mechanically shocked [6]. A possible explanation for these differences may be the different degrees of wetness and the variation in chemical concentration of the stack wall condensate, as measured by Berger et al. [7].

There is little doubt that there is no consistent field experience that points to a particular type of organic coating, much less a specific commercial formulation, that is best for general FGD use.

The situation from the standpoint of related laboratory work is not really any better. A commonly used evaluation technique involves the use of the Atlas Test Cell, in which coated substrates are exposed to refluxing scrubber liquor at an elevated temperature for a number of months and then the coating performance evaluated by examination for any visual changes, blistering or cracking of the material, followed by simple mechanical tests to determine adhesion [8]. Berger et al. [9] has reported on Atlas Test Cell evaluations for a number of commercial coatings, using the condensate from the chimney of an operating power station. On the basis of visual observations, microscopic examination, and solution analyses, the coatings were ranked in a performance rating, although no correlation with field experience was shown.

There has not been reported in the literature any well controlled evaluation of coatings under field conditions, until a study was made of commercial coatings on steel panels in the R. D. Morrow, Sr. plant near Purvis, MS by Battelle-Columbus Laboratories, in 1983. The coatings were carefully inspected after the completion of an 18-month exposure and detailed compositional and surface analyses made [6]. With this information the coatings were rated on their performance in protecting the steel against corrosion.

At about the same time as the Morrow field test, a program for the evaluation of coating resins was being carried out at Lehigh University. This involved laboratory testing in which a number of coating resins was exposed to dilute sulfuric acid for 1000-3000 hours and quantitative measurements were made on the coatings during the exposure. As a result of this effort, it was possible to rate the effectiveness of the neat resins for protection of the underlying steel against corrosion when exposed under laboratory conditions.

When the results of the Morrow field test and the Lehigh laboratory test programs were compared, it was found that there was good agreement in the results, both in the overall behavior of the coatings and in the modes of failure observed for the coatings that did not perform well, suggesting that the performance of the commercial coatings at the Morrow plant was very similar to the performance of the corresponding resin systems in the laboratory evaluation.

FIELD EVALUATION

The R. D. Morrow, Sr. Generating Plant located near Purvis, Mississippi, is one of the first limestone FGD systems that operated in a closed-loop mode. Reheat of the scrubber flue gas is provided by mixing with hot untreated flue gas. These operating conditions have created an environment in the outlet ducting and stack which is extremely aggressive towards most materials of construction. Since closed-loop systems are expected to be common in presently operating and future FGD systems, the severe conditions that are observed in the outlet ducting and stack of the R. D. Morrow Plant have been of major concern to the utility industry.

The FGD system of the R. D. Morrow Plant is a limestone scrubbing system which consists of a vertical tower with stages of Type 316 stainless steel rod decks to provide increased contact area between the flue gas and the counter sprayed limestone slurry. The wet-scrubbed gas at 54°C (129°F) and untreated hot gas at 150°C (300°F) are mixed in a vertical rectangular outlet duct. As shown in the schematic drawing in Figure 1, the wet gas

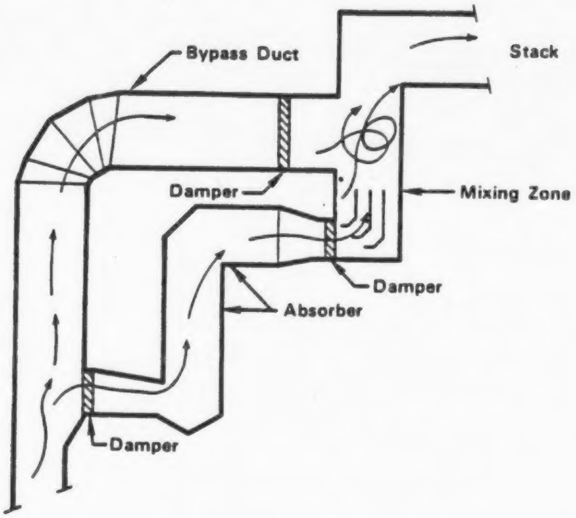


Figure 1. Schematic drawing of R. D. Morrrow, Sr. Generating Station Unit 1 or 2.

enters the duct approximately 5m (16 ft.) above the duct bottom. After mixing, the temperature of the wet gas is increased to approximately 60°C (140°F). The gas goes through a breeching to a stack where it is released to the atmosphere. There is a separate scrubber module, outlet duct and brick flue for each of the two units. Both flues are, however, in a common stack shell.

Nine different linings were exposed to the mixing zone environment of Unit 1 for 18 months. Table 1 provides a generic description for six of the organic linings studied. A detailed description of these linings and of their application procedures is given elsewhere [7].

The surface treatment of the carbon steel substrate was a grit blast with silica sand (8/35 mesh) and G-16 steel grit to a 100-150μm (4-6 mil) profile.

After surface treatments, the various linings were applied in approximately 0.7m (2.5 ft.) wide vertical strips from the bottom to the top of the outlet duct. During scheduled outages after 6, 12 and 18 months, the linings were visually inspected. Table 1 lists the appearance of the coatings after the 18-month exposure in the mixing zone. Of the six organic coatings, three held up quite well (A, B and C) and three showed gross failures (D, E and F). Figures 2 and 3 show blistering of the fluoroelastomer and one of the epoxies (D). During the final outage after 18 months of exposure, two panels of each lining, including the carbon steel substrate, were removed for further laboratory analysis. These panels were removed from the lower

TABLE 1. TEST LININGS IN THE OUTLET DUCT OF R. D. MORROW, SR. GENERATING PLANT UNIT 1

Lining Desig.	Generic Description	Application	Nominal Thickness mm (mils)	Appearance after 18 Months' Exposure
A	Glass flake reinforced vinyl ester	Spray applied; 3 coats	1.32-1.78 (52-70)	Cracking only at welds
B	Alumina and glass powder reinforced multifunctional epoxy w/graphite filler	Roller applied; 1 coat	0.64-1.02 (25-40)	Some pitting of steel
C	Glass flake reinforced modified epoxy	Trowel applied; 3 coats	1.15-1.34 (34-55)	Cracking only at welds
D	Alumina and glass powder reinforced modified epoxy	Trowel applied; 1 coat	0.4 (15)	Complete failure/ blisters
E	Fiberglass reinforced polyester	Roller applied and hand layed up	.4 (15)	Delamination
F	Fluoroelastomer	Spray applied; 8 coats	0.94-1.09 (37-43)	Severe blistering

duct wall section opposite the absorber outlet and the duct wall section opposite the bypass duct. The results of these laboratory analyses are presented elsewhere [11].

Reproduced from
best available copy.

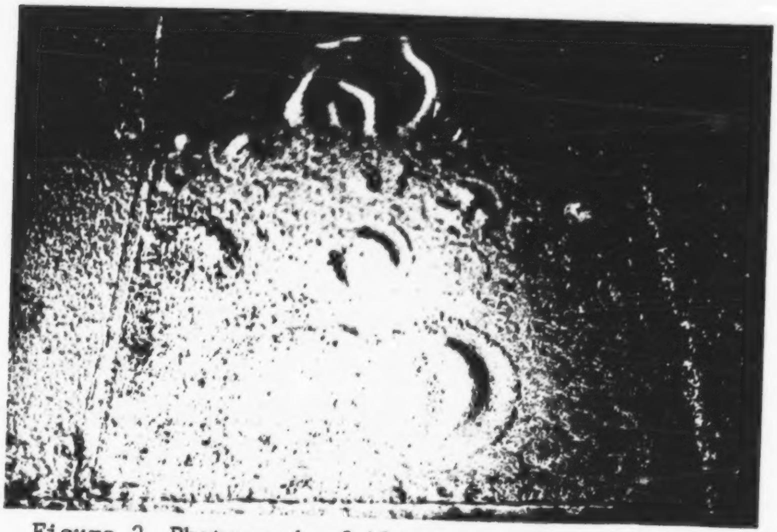


Figure 2. Photograph of blisters in fluroropolymer lining in the lower section of the vertical duct wall.

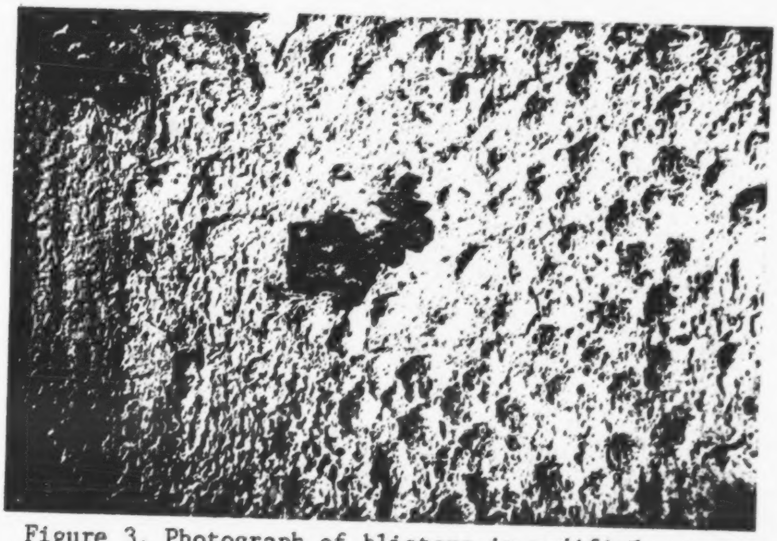


Figure 3. Photograph of blisters in modified epoxy lining D.

LABORATORY EVALUATION

In this program, four types of resins commonly used in formulating commercial coatings were applied to cold-rolled carbon steel and then exposed to 0.1M (1%) sulfuric acid at 60°C under isothermal conditions. The coating materials chosen were a fluoropolymer, a vinyl ester, a polyester, and three types of epoxies. During this exposure, measurements of coating properties and visual evaluation of the corrosion of the underlying steel were made. The measurement techniques used were corrosion potential, AC conductance, tensile adhesion, and weight gain. The details of materials, sample preparation and the exposure and measurement techniques have been given in previous papers [12,13]. Table 2 lists the values for each parameter that was found to be associated with either good or poor performance from the standpoint of protection of the underlying steel substrate. The values were chosen from the general relationships between the parameters and the observed corrosion after 1000 hours' exposure to 1% H_2SO_4 at 60°. The details of the selection of these values are discussed in the previous papers cited above [12,13].

TABLE 2. PARAMETER VALUES ASSOCIATED WITH COATING PERFORMANCE IN THE LABORATORY

Parameter	Units	Values Associated with Efficacy of Protection* Good Performance (G)	Values Associated with Efficacy of Protection* Poor Performance (P)
Corrosion Potential (E_{corr})	volts vs. SCE	> -0.6	< -0.6
AC Conductivity (Cond) at 2 kHz	S/cm	< 30	> 30
Tensile Adhesion	psi	> 0	0 (or cohesive failure)
Weight Gain	mg/cm^2	< 2	> 2 (or wt. loss)

---

*After 1000 h exposure to 0.1M H_2SO_4 at 60°C.

Table 3 shows the performance rating assigned to each of the resins studied, from the relationships shown in Table 2. The six coatings are divided into two groups--one where there was minimal corrosion of the steel, and the second where there was considerable corrosion observed. The evaluation of substrate corrosion was done by a visual examination after acid exposure. Since none of the four parameters shows a perfect correlation with coating performance, there are some apparent inconsistencies in Table 3. For example, the novolac epoxies which showed minimal substrate corrosion had a "poor" (low) corrosion potential value for the aliphatic/-aromatic amine cured material; in addition, the aromatic amine cured material had "poor" (high) conductivity values.

TABLE 3. LABORATORY EVALUATION RESULTS AFTER 1000 h IN 1% H_2SO_4 AT 60°C

Resin	Performance Rating			
	E_{corr}	Cond.	Adhesion	Weight Gain
	Minimal Substrate Corrosion			
Vinyl Ester	G	G	G	G
Novolac Epoxy				
Aliphatic/Aromatic Amine Cure	P	G	G	G
Aromatic Amine Cure	G	P	G	G
Fluoropolymer-Baked at 100°C/2 days	G	G	P	G
	Considerable Substrate Corrosion			
Bisphenol A/Polyamide Amine Cured	P	P	P	P
Polyester	G	P	P	P
Fluoropolymer RT Cure	ND	ND	P	P

ND = not determined.
G = Good performance
P = Poor performance

The results in Table 3 show that the steel coated with vinyl ester, the two novolac epoxies and the baked fluoropolymer showed minimal corrosion, whereas the polyamide amine cured epoxy, the polyester and the room temperature cured fluoropolymer coatings showed a significant amount of substrate corrosion. Figure 4 shows a blister that developed in a fluoropolymer sample during the laboratory exposure to acid.

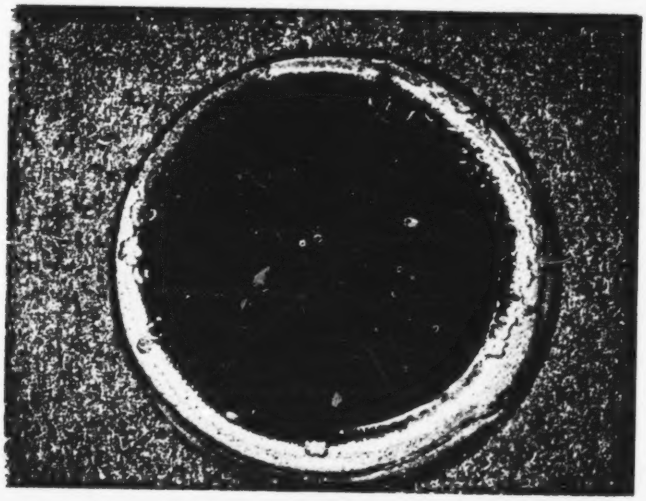


Figure 4. Photograph of blister developed in fluoropolymer during laboratory acid exposure.

COMPARISON OF FIELD AND LABORATORY DATA

Table 4 lists the coatings used at Morrow and the corresponding resin types, along with the performance evaluation, taken from Tables 1 and 3, for the Morrow and laboratory testing, respectively. Also shown is the mode of failure for each of the tests. The listing is in order of generally decreasing performance.

The performance rating (third and fourth columns) was summarized to indicate either "good" (G) or "poor" (P) performance. For the field testing, the "poor" performance was taken to be the coatings that showed complete failure, blistering, or delamination (Table 1). For the laboratory

TABLE 4. COMPARISON OF FIELD AND LABORATORY DATA

Coating at Morrow	Base Resin	Performance		Mode of Failure	
		Morrow	Lab	Morrow	Lab
A	Vinyl Ester	G	G	Cracks at welds	None
B	Novolac/Alip./Arom.	G	G	Pitting	Slight Corrosion
C	Novolac/Arom.	G	G	Crack	Slight Corrosion
D	Bisphenol A/Polyamide	P	P	Blistering	Blistering
E	Polyester	P	P	Cohesive Failure	Cohesive Failure
F	Fluoropolymer	P	P*	Blistering (Gas-Filled)	Blistering (Gas-Filled)

---

*Cured at room temperature.
G - Good performance
P - Poor performance

The vinyl ester and the novolac epoxies showed the best performance of the six coatings tested in both the laboratory and the field.

All three coatings that showed poor performance at Morrow behaved similarly in the laboratory testing. More importantly, the modes of failure were the same for each of the coatings: blistering for the bisphenol A/polyamide and the fluoropolymer (cured at room temperature), and cohesive failure for the polyester.

Of particular interest was the behavior of the fluoropolymer. In laboratory testing, the performance of the room temperature cured material was poor (blistering and high weight gains). However, when the material was baked (100°C for 2 days) following the room temperature cure, there was no blistering and also low values for weight gain. This was the only coating that was applied from a solvent (methyl ethyl ketone); it is likely that with only a room temperature cure there is some residual solvent remaining in the coating which gradually comes out of the material during acid exposure, resulting in the development of additional porosity which leads to more rapid permeation of acid to the substrate. This was undoubtedly the state of the coating in the field trial, where it received only an ambient cure. Thus, it performed poorly.

CONCLUSIONS

The good agreement between the results of the long-term field test and the short-term laboratory test lends credence to the concept that the latter testing can be useful in evaluating and predicting the behavior of organic coatings under actual operating conditions. The results also support the concept that the most important component of a coating is the resin that is used as the base material in formulating the final coating. The addition of fillers and pigments may slow down the attack of either the resin or the underlying steel, but the basic failure mode is the same in the field as in the laboratory.

ACKNOWLEDGEMENTS

The authors express their appreciation to the Electric Power Research Institute for their support of both phases of this work and to Barry C. Syrett and Charles E. Dene, in particular, for many helpful discussions.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

REFERENCES

1. G. H. Koch, N. G. Thompson, and J. Means, "Trace Elements in Flue Gas Desulfurization Environments and Their Effects on the Corrosion of Alloys," Corrosion/84, New Orleans, LA, April 1984, Paper No. 29.

2. N. G. Thompson, G. H. Koch, J. M. Spangler and B. C. Syrett, "Delamination of Solution Species that Significantly Affect Corrosion of Alloys in FGD Systems," Proceedings of 1984 Air Pollution Seminar on Solving Corrosion Problems in Air Pollution Control Equipment, Orland, FL, December 1984.

3. F. M. Mansfeld, D. O. Raleigh, K. Fertig and S. Jeanjaquet, "The Effects of Trace Elements in Corrosion Behavior in Total Immersion and Wet/Dry Conditions," Corrosion/85, Boston, MA, March 1985, Paper No. 38.

4. H. S. Rosenberg et al., "Construction Material for Wet Scrubbers: Update," EPRI Report CS-3350, July 1984.

5. E. R. Dille and W. C. Martin, "Stack Liners and Stack Corrosion on Wet Scrubber Systems," Paper presented at the American Power Conference, Chicago, IL, April 29, 1981.

6. R. C. Forsythe, F. K. Hirt, and W. E. Richards, "Chimney Liner Experience at the Bruce Mansfield Plant," Paper presented at the American Power Conference, Chicago, IL, April 26-28, 1982.

7. D. M. Berger, R. J. Trewella, and C. J. Wummer, "Evaluating Linings for Power Plant SO_2 Scrubbers," Power Engineering, Nov. 1980.

8. ASTM STP837. Manual of Protective Linings for Flue Gas Desulfurization Systems, 1984.

9. D. M. Berger, R. J. Trewella, and C. J. Wummer, "Evaluation of Linings for SO_2 Scrubber Service, J. Coat. Tech. 54, 47 (1982).

10. G. H. Koch, C. W. Kistler, W. Mirick, and C. E. Dene, "Evaluation of Linings in the Mixing Zone of the R. D. Morrow, Sr. Generating Plant," Paper presented at the 1984 Air Pollution Seminar, Orlando, FL, Dec. 5-7, 1984.

11. G. H. Koch et al., "Materials Evaluation in the Mixing Zone of R. D. Morrow, Sr. Generating Station," EPRI Report to be published.

12. M. L. White, H. Leidheiser, Jr., H. Vedage, "Laboratory Evaluation of Organic Coatings on Steel for Use in Acid Environments," Paper presented at the 1984 Air Pollution Seminar, Orlando, FL, Dec. 5-7, 1984.

13. M. L. White and H. Leidheiser, Jr., "Laboratory Studies of Organic Coatings in FGD-Type Environments," Paper presented at Corrosion '85, Boston, MA, March 25-29, 1985.